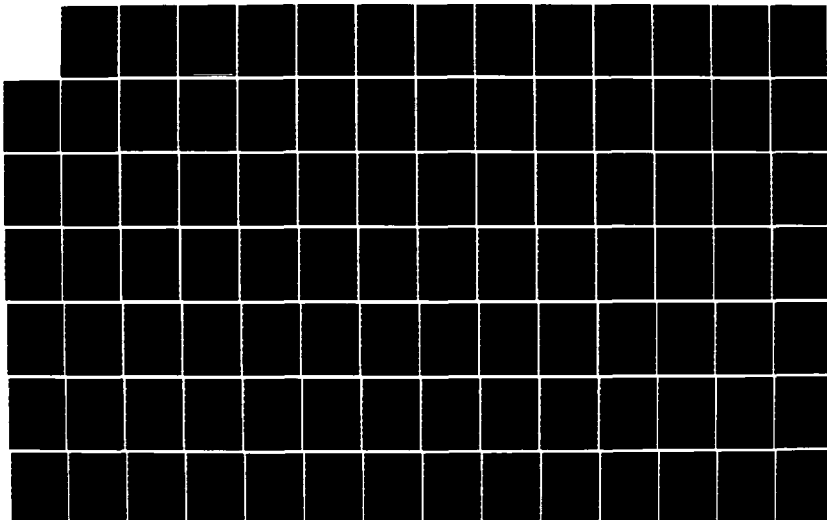AD-A173 894   SOURCES OF ERROR IN ACCELERATED STABILITY TEST METHODS   1/2
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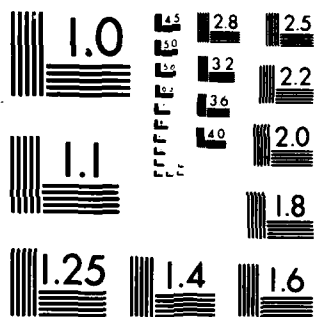UNCLASSIFIED   BFLRF-197 DAAK70-82-C-0001   F/G 14/2   NL

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	1.25	1.4	1.6

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SOURCES OF ERROR IN ACCELERATED STABILITY TEST METHODS FOR DIESEL FUELS

INTERIM REPORT
BFLRF No. 197

By

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Ten test methods (including ASTM D 2274) used to determine the accelerated oxidation stability of middle distillate fuels were reviewed. A critique of various procedures (such as weight and volume measurements) within these test methods was written, including an estimation of which procedural steps had the greatest effect on the final test results. Subsequent laboratory work allowed more definitive conclusions to be made on the effect of particular preaging, aging, and post-aging procedures on test results using a small set of test fuels.

Changes in the particulate filtration procedure and adherent fuel insolubles determination were incorporated into a new test method which was cooperatively "round-robin" tested. A summary of these data are also included in this report. Precision data suggest that this method is an improvement over that of the standard D 2274 test method.

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FOREWORD

This work was performed at the Belvoir Fuels and Lubricants Research Facility (SwRI) (formerly U.S. Army Fuels and Lubricants Research Laboratory), Southwest Research Institute, under DOD Contract Nos. DAAK70-82-C-0001 and DAAK70-85-C-0007. The project was administered by the Fuels and Lubricants Division, Materials, Fuels, and Lubricants Laboratory, U.S. Army Belvoir Research, Development and Engineering Center, Fort Belvoir, Virginia 22060-5606, with Mr. F.W. Schaekel, STRBE-VF, serving as Contracting Officer's Representative. This program was funded by the U.S. Navy David Taylor Naval Ship Research and Development Center with Mr. R. Strucko, Mobility Fuels Group, Code 2759, serving as Technical Monitor. This report covers the period of performance from 31 October 1983 to 31 May 1985.

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I. INTRODUCTION AND BACKGROUND

The initial impetus for this program was prompted by two concerns. The first was a U.S. Navy concern regarding adequacy of acceptance criteria for fuel stability. The second came from a request of the Quadripartite Navies (which includes the U.S. Navy) to the American Society for Testing and Materials (ASTM) Committee D02 (on petroleum and petroleum products) in April 1983 (see Appendix A) to "improve or replace" the existing ASTM D 2274 accelerated stability test procedure. Thus, a program was developed to establish an understanding of the factors affecting the severity, repeatability, and reproducibility of accelerated aging procedures for middle distillate fuels.

The Navy-Coordinating Research Council Barge Storage Program (1a-1b)* (conducted in the 1950's to determine the scale-down factor from barge to bottle or drum-storage) provided data indicating the usefulness of storage at 43°C (110°F) as a predictive indicator for long-term storage stability. With the accumulation of additional data, many researchers have accepted the results of aging fuels at 43°C for 13 weeks to be approximately equivalent to drum or bottle storage at ambient temperatures for one year.(2-7) Although the ASTM has accepted several accelerated tests for evaluating petroleum products, only the "Test for Oxidation Stability of Distillate Fuel Oil (ASTM D 2274-80)" is directly applicable to middle distillates.(8) The current ASTM D 2274 procedure requires oxygen to be bubbled at the rate of 3 L/hr through a sample for 16 hours at 95°C. The filterable insolubles are collected using a glass-fiber filter while the adherent fuel insolubles are removed with the use of a solvent. The quantity of both insolubles is determined gravimetrically. This test has the most industry-wide acceptance and has been a requirement in both military and federal fuel specifications for many years.

The ASTM D 2274-80 accelerated stability technique is currently specified in Federal Specification VV-F-800C (for diesel fuel oil) and MIL-F-16884H (for Naval distillate fuels) as a measure of storage stability for bulk fuel deliveries at the time of procurement. These specifications have a D 2274

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

acceptance limit of 1.5 mg of total insolubles in 100 mL of sample. However, the stated repeatability of ASTM D 2274 in the range of 0 to 1 mg/100 mL is 0.3 mg/100 mL, while the reproducibility is 1.0 mg/100 mL. Statistical data developed in 1978 in the range of 1 to 5 mg/100 mL gave a repeatability of 0.9 mg/100 mL and a reproducibility of 3.0 mg/100 mL. With such a broad range for precision and reproducibility, it is difficult to accurately assess fuel quality in the 1.5 mg/100 mL range.

A 2-year project (9) sponsored by the Department of Energy (DOE) studied the formation of deleterious products in middle distillate fuels in an effort to develop more reliable test methods for fuel stability. During the first year of that program, eight accelerated stability tests were chosen and evaluated using a set of six test fuels. Accelerated stability test results were then related to test results obtained at a storage temperature of 43°C (110°F). Overall, the stability data from the 43°C storage did not follow a trend which was directly predictable by any one of the other test methods; however, the data from an 80°C test served this purpose best.

During the second program year, primary emphasis was placed on further development of standarized 43°C and 150°C tests in cooperation with ASTM and on the testing of eight additional fuels. These eight fuels had a wide range of stabilities providing data which, when mathematically correlated, allowed for a number of observations. Total insolubles, as opposed to total gum weights, were judged to be more acceptable for data correlation since total gum weights could not be reliably corrected for initial gum weights. Test results using 43°C, 80°C, 150°C, and ASTM D 2274 provided directional agreement. Vented versus nonvented storage at 43°C did not provide any evident bias related to test configurations at the 4-, 8-, 12-, 18-, and 24-week test intervals. No significant bias could be found for various bottle compositions and configurations in the 43°C test. In an effort to standardize the 43°C and 150°C tests, planning and cooperative testing were provided to ASTM Committee D 02.E0.05 (Distillate Fuel Stability and Cleanliness).

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A better understanding of the parameters involved in accelerated stability testing of diesel fuels was still needed and is partially addressed in the program described in this report.

The program covered in this report was divided into five phases which included:

Phase I: Background Review and Assessment
Phase II: Evaluation of Preaging Procedures
Phase III: Evaluation of Aging Procedures
Phase IV: Evaluation of Post-Aging Procedures
Phase V: Application of Program Results

These same phases are used in the text of this report.

II. PROCEDURE

Initial work under Phase II was accomplished using a Jet A fuel filtered through 0.2-μm mixed cellulose ester screen filters. Later work in both Phases II and III (where the effects of heat stress were monitored) involved four test fuels. These fuels are described in Table 1. The abbreviated nomenclature of each fuel in Table 1 is used throughout this report. While none of the fuels in Table 1 is a MIL-F-16884H (F-76) specification fuel, the fuels were chosen to cover a broad stability range and are similar in many of their properties to F-76 specification fuels. The LCO Blend and DF-2 fuels were provided by Naval Research Laboratories (Washington DC) where additional tests and evaluations were being performed.

TABLE 1. TEST FUELS

Abbreviated Nomenclature	Description
Cat 1-H	Caterpillar 1-H/1-G engine reference fuel (reference)
1%S	1 percent sulfur referee diesel fuel (MIL-F-46162B)
LCO Blend	Blend of 70 percent straight run (NRL 82-8) fuel with 30 percent catalytically cracked percent light cycle oil (NRL 83-52)
DF-2	DF-2 from Conway, Arkansas (VV-F-800C specification) (NRL 83-40)

The LCO Blend fuel was mixed immediately prior to experimental use.

Particle distributions (size and number) were obtained using a HIAC-Royco Model PC 320 with a LAS 346 laser source. The principal of operation was that of single particle light blockage. The particle diameter channels used in this study were 0.5-0.8, 0.8-1.0, 1.0-2.0, 2.0-3.0, 3.0-5.0, and >5.0 μm. The experimental test procedure and data are provided in Appendix B (Particle Distributions) as these data did not lend themselves to a definitive discussion within the main text of this report.

Table 2 provides the physical/chemical properties for the test fuels listed in Table 1 and used in this program.

TABLE 2. TEST FUEL PROPERTIES

	Cat 1-H	1% S	LCO Blend*	DF-2*
Cetane No., D 613	51	43	ND	ND
Cetane Index, D 976	48	43	43	46
Visual Appearance, D 4176	Clear/ Bright	Clear/ Bright	Clear/ Bright	Clear/ Bright
Water and Sediment, D 2709, vol%	ND	ND	ND	0.002
Distillation, D 86, °C				
50% evap.	272	276	276	256
90% evap.	324	339	339	302
End Point	350	371	360	330
Residue plus loss, vol%	1.5	1.0	3.5	1.5
Flash Point, D 93, °C	88	62	>60	77
Pour Point, D 97, °C	-13	-23	ND	-31
Cloud Point, D 2500, °C	-9	-18	ND	-21
K. vis., 40°C, D 445, cSt	3.1	2.9	ND	2.3
Carbon Residue, 10% Bottoms, D 524, mass%	0.10	0.13	ND	0.05
Sulfur, mass%	0.42	1.05	ND	0.40
Copper Corrosion at 100°C, D 130	1A	1A	ND	1
Ash, D 482, mass%	<0.010	<0.001	ND	0.003
Gravity, °API, D 1298	34.5	31.2	31.1	35.0
Demulsification at 25°C, D 1401, minutes	ND	ND	ND	2
Acid Number, D 974, mg KOH/g	0.03	0.02	ND	0.02
Neutrality, FED-STD-791 Method 5101	ND	ND	ND	Neutral
Accelerated Stability, D 2274, Total Insolubles, mg/100 mL	1.2	1.7	2.4	3.1

ND = Not Determined
* Data supplied by Naval Research Laboratories, Washington, DC

A description of the other experimental procedures used in the various phases is included with the results and discussions in order to facilitate report continuity.

III. RESULTS AND DISCUSSION

A. Phase I: Background Review and Assessment

Prediction of fuel storage stability using accelerated aging conditions has been shown to yield poor precision in the region where insoluble gum formation limits have been established (10) (e.g., MIL-F-16884H which requires an ASTM D 2274 value of 1.5 mg/100 mL). In an attempt to determine where the major sources of error could occur, several commonly used tests were reviewed, including the following: (9-15)

1. duPont F 21
2. duPont F 31
3. Nalco 300°F
4. EMD-Diesel Fuel Stability
5. Union Diesel Blotter
6. UOP 413-82
7. DEF STAN 05-50/1
8. ASTM D 873
9. ASTM D 2274
10. ASTM Proposed 110°F (43°C) Test

An estimate of the potential influence on the final test result, through lack of precision or accuracy of each step, has been made. A computer-based literature search was conducted through the American Petroleum Institute (API) data base to identify pertinent research that had already been conducted. In addition, several researchers in the field of middle distillate fuel storage stability were contacted for their input on the current state of accelerated oxidation test procedures.

The following sources of error (Items 1-17) are covered as general topics since they are steps in many of the recognized accelerated stability tests and are not necessarily restricted to any particular test. Table 3 provides an overall summary of the 16 procedural steps identified for discussion. This

TABLE 3. SUMMARY OF POSSIBLE ERROR SOURCES IN PROCEDURAL STEPS

Procedural Step	Potential Problem	Effect on Final Result	Recommendation
1. Cleaning and rinsing of glassware	Adsorbed materials or altered container surface may alter reaction sites.	Could alter the results in any direction.	Be more specific in cleaning and rinsing instructions/procedures.
2. Choice of glassware type	Surface effects	As above	Use borosilicate glass for all aging procedures.
3. Volumetric measurements	Inaccurate amount of fuel taken to be aged and/or filtered.	Minimal if reasonable techniques and care are taken.	Do not change this part of the procedure.
4. Gravimetric measurements	Inaccurate weight of filter/gums.	Minimal if reasonable techniques and care are taken.	Do not change this part of the procedure if up-to-date equipment is being used.
5. Effect of light	Reaction kinetics enhanced by non-thermal energy source.	Increase the amount of gums formed, possibly significantly.	Be more specific in instructions/procedures for shielding samples from light.
6. Sample preparation	Filtration removes particulates which are potential reaction sites.	Overall reaction sequences may be altered however, if not filtered samples may begin test	The difference, if any, between results using filtered and unfiltered samples should be determined on different basis.
7. Heating baths	The time required to obtain test temperature is different between air and liquid bath.	In high temperature (short duration) tests the variation in sample temperature could be significant.	Determine actual affect on test results for various temperatures to see if delay time does cause significant changes.
8. Introduction of O_2 to the test system	The mode of introduction of O_2/air into the test system can cause significant differences in test results.	Significant variations could be obtained between laboratories depending on how gas flow is delivered to sample.	Be specific in method of gas delivery as described in test protocol making sure that bubble size and rate are repeatable.
9. Type of filter paper	Retention of particulates may not be the same from one filter to the next.	Weights of particulate matter retained could vary significantly.	Determine how filtration varies and make appropriate recommendations as to best paper type and procedure.
10. Fuel removal	On occasion the solvent may cause a floc to form which can be trapped on the filter.	A significant weight increase may occur which is not caused by the aging process.	Note in the procedure that this may occur and for the experimenter to be aware if it does occur. Determine the cause of floc formation and find appropriate remedy.
11. Adherent gum removal	Some gum may remain on test container.	Weight of adherent gums may be significantly lower than it should be.	Determine a more universal solvent which will remove all gums formed.
12. Air/steam jet evaporation	Solvent/fuel evaporation takes place at a higher temperature than the test temperature.	Possible increased gum formation.	Experiments have shown that this type of evaporation technique does not affect final results. No changes are apparently necessary.

TABLE 3.   SUMMARY OF POSSIBLE ERROR SOURCES IN
PROCEDURAL STEPS (CONT'D)

Procedural Step	Potential Problem	Effect on Final Result	Recommendation
13. Sample cooling time/rate	Number and size of particulates formed may vary depending on cooling conditions.	Filterable particulates may change significantly thus causing a variation in deposit on the filter.	Determine variability of particulate size and number as a function of cooling rate and time.
14. Temperature of test	Predominant reactions may vary as a function of temperature.	The linear extrapolation required for prediction of ambient storage potential may not be valid.	Continue studies of kinetics and energies of activation to determine the maximum temperature to which a fuel may be exposed and have kinetics reflect those at ambient temperature.
15. Reflectance	Calibration and interpretation of measurements may vary between personnel.	Same sample may be interpreted in different ways.	Employ proven instrumental methods rather than visual interpretation.
16. Personnel	Physical or mental variability	Not predictable	Training should be as rigorous as the usefulness of the results warrent. Periodic retraining should be part of the program. Intercommunication with other laboratories concerning uniformity of operations.

general discussion is then followed by an error assessment summary which was used as background to the evaluation phases of this program.

1.   Sources of Error

1.   Cleaning and Rinsing Glassware--Cleaning procedures for glassware used in the various oxidation stability tests are usually not described adequately. Factors to consider in this regard are (a) the time elapsed since last cleaning, (b) storage environment since last cleaning, (c) potential for residual contamination, and (d) potential for surface changes during cleaning (e.g., ionic residue, etching, scratching, etc.)

Any of these factors could significantly affect the duration of any induction period, which could dramatically affect the test results.(16) Used containers are often cleaned with chromic acid cleaning solution. It is well known that the chromate ion adheres strongly to the surface of glass. Tests have shown that approximately 30 simple rinsings with water (i.e., filling the container and then emptying it) are required to remove all traces of chromate.(17) The removal of chromate can more easily be accomplished by a continuous jet of water entering the mouth of an inverted glass container in such a way that the water hits the top and drains down the sides.

Usually, depending on the size of the container and the water flow, removal of all chromate can be accomplished in less than 2 minutes. This faster technique cannot easily be applied to the washing of all containers; thus, the more time consuming practice is usually required. Similar problems may also apply to other surface adsorptive cleaning agents. For this reason, nonmetal cleaners should be used to eliminate this potential problem. Also, for consistency, new and used glassware should be cleaned similarly before use.

2.   Glassware--Christian, et al. (18) studied the effect of glass surfaces with respect to distillate fuel stability using fuels in the No. 2 burner oil and diesel fuel volatility range. They found that soft glass had an inhibitory effect on the degradation of many fuels, but borosilicate glass was essentially inert. Their tests, which used various size containers (1 liter

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and 500 mL with the borosilicate glass; one pint and one quart with the soft glass) and a constant amount of fuel (350 mL) showed that container size had no appreciable effect. These tests demonstrated that other variables, such as the amount of air in the container above the fuel and the area of the air-fuel interface, were not limiting factors. When the surface area in contact with the fuel was doubled, the rate of degradation in the soft glass containers was markedly decreased. No significant effects were observed where the borosilicate glass containers were employed. These researchers concluded from this limited study that fuel storage in soft glass bottles can be misleading as to the relative stability of distillate fuel. They found borosilicate glass to be essentially inert and much more satisfactory for these tests. Also the borosilicate glass should have a much closer similarity to large tank field storage when the surface to volume ratio is very small. Since most of the accepted accelerated stability techniques specify borosilicate glass, the use of this glass should have a minimal effect on the results. However, the researcher should be aware of the potentially misleading results which could be obtained using soft glass.

3. Volumetric Measurements--Volumetric glassware obtained from a reliable manufacturer is usually sold under definite specifications with regard to tolerances (maximum allowable errors). Practically all chemical glassware sold in the United States is calibrated for use at 20°C. When such apparatus is used at temperatures other than 20°C, a correction is usually in order if accurate results are desired. When the volumetric apparatus has a content of 100 mL or less and the room temperature is within 5 degrees of 20°C, this correction is negligible.

Errors, usually relatively small, can occur when taking volumetric readings. Many of the methods for measuring oxidation stability use volumetric measurements at some step in the procedure. All liquids, when placed in a container, form a meniscus at their upper surface. When liquids are transparent, accurate readings are best obtained by noting the lowest point of the meniscus. Parallax errors can occur when taking such readings if the eye is not close to the level with the meniscus. Procedures have been developed for eliminating this type of error.(19)

4. **Weighing**--Analytical weighing with today's sophisticated balances does not require the tedious procedures and sometimes inaccurate results that may have resulted in the past. In fact, analytical weighings have become almost routine. Although many of the oxidation stability tests require several weighings in their procedures, weighing errors should be almost nonexistent as long as manufacturer recommendations and standard procedures are observed. Any significant errors made through negligence should surface immediately when duplicate tests are compared. Table 4 indicates potential errors of weighing assuming readability and precision are similar. However, experience in certain laboratories has shown that the readings in Table 4 might actually be a best case situation and, in reality, the error may be at least a factor of 2 greater.[20] Filter handling and environmental effects (e.g., humidity, electrostatics, temperature stability, etc.) are potentially more important factors than the weighing errors based on weighing balance readability and precision alone. These considerations become even more important in the weighing of wall adherent insolubles in the gum beaker procedure. Other factors which relate to the accuracy of the test are given in Item 17.

TABLE 4. POSSIBLE ERROR OCCURRING WITH A SINGLE WEIGHING*

| | | Filterable Insolubles | | | |
| | | 0.5 mg/100 mL | | 1.5 mg/100 mL | |
	Sample Volume (mL)	Sample Wt	Percent Error	Sample Wt	Percent Error
duPont F21, Nalco 300°F, EMD-Diesel Fuel Stability, Union Diesel Blotter	50	0.25	40	0.75	13.3
DuPont F31, ASTM D 873	100	0.5	20	1.5	6.7
UOP 413-82	150	0.75	13.3	2.25	4.4
ASTM D 2274	350	1.75	5.7	5.25	1.9
DEF STAN 05-50/1	700 ±10	3.5	2.9	5.25	0.95
43°C Test	1000	5.0	2.0	15.0	0.67

*Electronic balance with a readability of 0.1 mg.

5. **Light Effects**--In almost all the accelerated test methods for storage stability, there are no definitive procedures that describe the manner in which the sample should be shielded from light. The simplest of the photochemical systems are those involving the absorption of light by molecules and

the subsequent chemical reactions induced by these molecules.([21]) Trace amounts of photosensitizers, like naphthalene, phenanthrene, etc. can increase photochemical reactions by several fold.([22]) Aging of fuel by light is not uncommon. Schwartz, et al. ([23]) discussed the accelerated aging of gasoline by ultraviolet irradiation in the early sixties. They noted an overall weight gain in every irradiation they conducted. This was attributed to the reaction of the test fuel with oxygen, which was substantiated by elemental analysis of the gum and distillate.

Por ([24]) compared product degradation induced by accelerated oxidation and ultraviolet procedures. He found that in all cases there were significantly higher deposit formations when the gas oil samples were irradiated, while the gum formation was usually lower. Only in the presence of certain components in the gas oil, having a specially high gum-forming tendency, were gum formations higher by irradiation of the samples.

6. Sample Prefilter Versus Use as Received--The condition of the sample when submitted for analysis could have an effect on the final results. Two philosophies have been expressed concerning sample preparation. One is that the sample should be examined as received since that is the condition of the fuel in storage; therefore, that is the mode in which the fuel should be tested. The other thought is that if a fuel is not filtered, the particulate matter (both organic and inorganic) could act as a reaction promoter (catalyst). In addition, the comparison of aged fuel to initial fuel would be much more difficult. Thus, by filtering the sample, all tests would start on an equivalent basis.

Insufficient data on petroleum-based fuels are currently available to make a definitive statement as to whether a fuel should be filtered or not prior to testing. Whether or not the test fuel is prefiltered could potentially be a major factor in directing the final test results. If should be noted that most field evaluations of fuel stability do not involve prefiltration.

Extensive data are available for certain coal-derived fuels ([25]), in particular H-coal, naphtha, EDS middle distillate, and blends of coal and petroleum-derived naphthas. In general, elemental analyses do not change, nor does the specific gravity. However, soluble gum values appear to increase,

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while precipitate and adherent gum formations appear to decrease in the filtered samples during a 43°C aging process.

7. Heating Baths--The thermostated reservoir fluid required to maintain the samples at test temperatures can be either liquid or air depending on the particular procedure employed. The concern here is the time required for the test specimen to reach the test temperature. Most tests operate with a specific time/temperature protocol. This could pose a potential source of error in that a finite time is required for the samples to reach test temperature. This could be significantly longer in air than in water or oil due to heat transfer rate differences, sample agitation, etc. It has been observed that 150 mL samples reach 80°C from room temperature in approximately 1 hour using a liquid bath but requires at least 2 hours in an air bath. Formation of the insoluble gums thus would be greater the more rapidly the test temperature was achieved. Calibration of these baths with certified thermometers should be a matter of routine.

8. Gas Flow Metering Versus Sample Agitation--Por (24) has shown that there is a significant difference in product formation if O_2 is bubbled through the sample from an open tube or through a sintered glass filter. The smaller bubbles cause greater contact with the liquid and thus reactions can proceed at a more rapid rate. The use of air rather than oxygen showed insignificant differences as long as flow was normalized to the O_2 content. As an extension of this finding, it would appear that shaking air in contrast to pure O_2 into a sample and leaving it vented, but otherwise undisturbed, would further minimize oxygen available for reaction, thus causing less product to form. This would, however, depend on O_2 solubility and rate of uptake. Concern should also be addressed to reactive volatile species lost due to gas purging versus nonvented testing.

9. Filter Media--The type of filter media used to trap suspended particulates and the consistency of particle retention appears to be a significant factor in obtaining consistent final results. At least three investigators (26-28) have studied the variability of retention of filters in ASTM D 2274 (or D 2276) type tests. Rowland, using 0.8-μm membrane filters, showed that

both good precision and good reproducibility could be obtained. However, both Hiley and Westbrook, using glass fiber filters, found poor precision. In addition, Westbrook found that membrane-type filters were, in general, more retentive than corresponding nominal pore size glass fiber filters.

Since this is one of the critical points in the determination of insoluble particulate weights, it is apparent that an in-depth review of the type of filter specified for the test should be undertaken. This review should be considered not only because of variability between filters from the same batch but also from the standpoint of nominal pore size since the major portion of particulate matter may actually have diameters less than the specified nominal pore size. Reviews of the filtration process have been published (29-30) as has a theory of filtration (31). Related discussions will also be found in Items 13 and 17.

10. Fuel Removal Solvent--Entrained-trapped fuel must be removed from the gums to avoid apparent excessive weight which would distort the final results. Under normal circumstances, a nonpolar hydrocarbon solvent would be sufficient for this purpose. On occasion, addition of isooctane has caused a flocculant material to form in an otherwise apparently clear aged fuel sample.(32) Although this does not happen often, it could be a significant factor in the analysis of particular fuels which have high solvency. A study as to fuel characteristics and other factors which could cause this problem and a means to overcome the flocculant formation should be considered. As a minimum in the process of fuel filtration, solvent should not be used until the filter reservoir is essentially empty of fuel.

11. Adherent Gum Removal--Adherent gums are normally removed from the aging container with a tri-solvent system consisting of acetone, methanol and either benzene, chloroform, or toluene. The latter is chosen for its lower toxic potential. It is possible, depending on the length of time the gums have been exposed to the atmosphere, that the tri-solvent system will not remove all the adherent gums. It has been observed that dimethylformamide and dimethylsulfoxide will also leave a residue of adherent gum. Tetra-hydrofuran did remove the final noticeable traces of adherent gum, which

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amounted to approximately 25 percent of the total adherent gums removed.(31) An alternative procedure which could potentially eliminate this problem is a direct gravimetric analysis of the container before and after gum deposition.

12. Air/Stream Jet Evaporation--The boiling point of the test material dictates if air or steam jet evaporation will be used in the existent gum test. As long as the temperature specified by the test procedure is maintained, the conical adapters are kept clean, and foreign material prevented from getting into the tared beakers, the standard test method for existent gum in fuels (D 381) is straight forward. Duplicates could be run so that any introduced error in a single run would readily be revealed. Undetected errors resulting from this aspect of the test would then be very unlikely.

In the past, a number of investigators surmised that gum formation was caused by oxidation of the fuel during air-jet gum tests. Tests were conducted by the Bureau of Mines laboratories, using a conventional air atmosphere for evaporation, replacing the air with steam and then with nitrogen. The results from these tests showed that there was very little change in the amount of gum determined with any of the three atmospheres used, thus indicating that oxidation due to hot air/fuel interaction during the standard air-jet evaporation is not as great a factor as had been believed.(23) Alternatively, gum values determined using low temperatures under high vacuum may not be equivalent to air/steam jet gum.

13. Cooling Time/Rate--The time and rate of cooling of a liquid can cause a variation in the size and number of insoluble particles formed from solution. Thus far, a study of this phenomenon has not been reported. The importance of particle size is significant when considering that the filter used to trap these materials has a finite pore size. The pore size could, under certain circumstances, be inappropriate to secure a representative (or reproducible) sampling of the insoluble material. It is therefore possible to envision the same sample under one condition forming larger particles (e.g. $\sim$ 1-μm diameter) with most of the product trapped on the filter. The same filter (e.g., 0.8- or 1.2-μm nominal pore size) would permit most of the fine particles (e.g., $^{-}$0.5-μm diameter) formed under different conditions of cooling to pass

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through. This consideration also has raised the question as to whether very fine filtration (using multiple pass techniques through 0.45-μm filters) should be considered. The final temperature after cooling and the maximum time to arrive at that temperature should be described and adhered to, since particle agglomeration and solubility are both functions of temperature and equilibration time.

14. Test Time and Temperature--A number of times and temperatures have been suggested as a part of various protocols used to determine fuel stability through accelerated aging techniques. These temperatures range from 43°C (110°F) to 150°C (302°F) (33) with times from weeks to hours, respectively. In each case, the assumption is made that if the time is varied then the data would be on a line through zero time if the test temperature remained constant. A second assumption is then made when a correlation is required to predict the potential for satisfactory long-term bulk storage of the test fuel. This assumption is that it is possible to linearly extrapolate the formation of deleterious products determined in the accelerated test to other times and temperatures, particularly ambient storage conditions. If this were true, then, by inference of the Arrhenius equation, the energy required for product formation would be the same regardless of fuel type or experimental conditions.

A number of investigators have shown a wide variation in energy required for reaction (33-35) to take place in a fuel, thus showing that an extrapolation to ambient conditions for one fuel does not necessarily apply to another fuel. There is also increasing concern and some data that may show a change in predominance of certain reaction sequences in fuels as the temperature is increased. Further work is required to properly define these changes. However, should this be shown to hold true, then it is possible that a test temperature valid for one fuel may yield erroneous predictions for another fuel. Thus, a different accelerated aging temperature for each different fuel category would be required.

15. Reflectance--In several of the test methods for oxidation stability, colorimetric and/or reflectance evaluation are incorporated into the proce-

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dure. Filter pads in one of the test methods are often rated visually. Data indicate the filter pad rating can be repeated within ±0.5 visual rating number (±5 percent reflectance).(12) The reflectance rating technique in rating these filter pads is usually preferred to visual rating since it is more accurate. Visual ratings against reference standards are subjective and depend on the skill of the individual doing the rating. The color of the fuel before and after the test has variable significance depending on the requirements imposed.

16. Personnel--One factor that is variable without prediction is the human factor. The physical aptitude and particularly mental attitude of the person performing the test can vary from day to day in the same person and is generally different among people. In most cases, this difference would not cause a major variation in test results. Certain factors must be considered as potential causes for error. Among these are:

1. Personnel training on use of equipment (technique)
2. Interpretation of test procedures
3. Potential for misapplication of the above due to fatigue or mental attitude.

The potential error here may be reduced by requiring certification of those who will be applying the test and submission of periodic "blind" samples of material of known stability to check operator accuracy.

17. Other Factors--Volume and weight measurements are normally quite accurate only if the material being measured significantly exceeds the lower limiting weight/volume requirements of the measuring apparatus. This in turn means that, for fuels generating minimal quantities of gum, perhaps more fuel should be used in the test. Even though the weight of gum/100 mL fuel would remain the same, a greater quantity of gum would be formed, thus tending to minimize other potential errors (e.g., weighing, transfer losses, etc.).

Methods for equilibrating filters prior to weighing both before and after sample filtration can potentially lead to large weighing errors even to the

point of giving "negative" results. The method of filtration (vacuum, pressure, multipass, etc.) may also be a contributing factor to the amount of material retained on the filters. A more rigorous specification for filtration and weighing procedures may be required. Additionally, when weighing gum beakers to determine wall adherent insoluble values, errors associated with room environment (e.g., humidity, electrostatics, and, especially, temperature variation effects) and beaker handling need definition as large errors can be introduced from beaker weighing procedures.

2. Error Assessment Summary

The following areas of study were recommended in light of this review and in consideration of suggestions made by other researchers concerned with determination of diesel fuel accelerated stability. Areas of priority have been generally established with the items being discussed in the order of potential importance.

Area 1. The most significant problem associated with accelerated aging techniques is the gravimetric *determination of soluble gums*, insoluble particulate matter, and adherent gums. There are at least two possible methods by which this problem might be alleviated. The first is to use a more sensitive balance to weigh the filters and glassware, thus imparting a greater accuracy to the first (and second) decimal place. This does have a limitation on cost and total weight capacity of the balance. A potentially better method is to create a greater quantity of gum material to be measured, thus not stressing the lower weighing limits of existing balances. Therefore, it is recommended that methods to accomplish this end should be studied. In particular, the effect of using greater volumes of fuel during the test is recommended. This would also be accompanied by determination of the optimum container configuration. The effect of longer experimental aging times may also be significant and should be considered also.

Area 2. An experimental parameter which could have a major effect on the final results of an accelerated stability test is the size and growth rate of insoluble particulates. It is strongly recommended that cool-down temperature and duration prior to filtration and its effect on total amount of insolubles and on particle size distribution be studied in detail to determine

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if the filter type and pore size currently being used are sufficient to trap a representative portion of the particles. This would, in turn, have an effect on Area 1 above, especially if the weight of particulate matter trapped fluctuates due to variation in particle growth.

Area 3. The rate at which a sample achieves test temperature and the test temperature itself could be significant factors in the overall aging (gum formation) processes. The chemical kinetics of a system could drive a reaction to dominance at one temperature but would be of lesser significance at another temperature. Of major concern is that the maximum temperature that will truly reflect ambient storage conditions is not being used, and that product formation may or may not maintain the same energy of activation. It is, therefore, recommended that a study be made (perhaps in conjunction with Area 2 above) of the linearity of the Arrhenius plot for fuels of various saturate/aromatic ratios and heteroatom content to determine the highest temperature that still maintains a linear result. The slopes of Arrhenius plots for different fuels could be significantly different, also, and this would have a major influence on selecting a reliable stress temperature.

Area 4. The accurate determination of adherent gum is hindered by variable solubility in the normally suggested trisolvent system. It is recommended that a more comprehensive procedure for quantitative analysis of adherent gum be determined. This may be through either a more universal solvent or by gravimetric analysis without prior gum removal.

Area 5. The necessity of bubbling oxygen through the sample as required in certain aging tests should be studied to determine if it is indeed necessary and, if so, what are the optimum rate and bubble size. Additionally, loss of volatile reactive species in purged systems should be evaluated in relation to nonvented test systems.

Area 6. The effect of using filtered versus unfiltered fuel should be determined. If filtered fuel is required, the optimum filter pore size and type should be determined.

Area 7. Probably least important of the recommendations listed, but still a potential factor in causing variability in the final result, is to determine

the cause and correction of occasional flocculant formation when fuel being filtered is washed with a hydrocarbon solvent. In practice, solvent should not be used until all of fuel has left the filter.

B.   Phase II: Evaluation of Preaging Procedures

Weighing repeatability, filter efficiency, and effect of no prefiltration of test fuel were selected for evaluation as potential preaging procedural effects on test results.

    1.   Weighing Repeatability

In order to determine the effect of gravimetric analysis on the final results, repeated weighings of various filter types both before and after contact with fuel were performed. Glass fiber filters (0.7-, 1.2-, and 1.5-μm nominal pore size) and mixed cellulose ester screen filters (0.45-, 0.80-, and 1.2-μm pore size) were rinsed with isooctane and dried (60 min at 100°C for glass fiber; 30 min at 90°C for cellulose ester filters). The 22-mm diameter glass fiber filters were placed in a Gooch crucible. The cellulose ester filters had a 47-mm diameter with an effective filtration diameter of 35 mm.

Five filters in each size/type category were weighed five separate times. After these weights were obtained, 100 mL of prefiltered Jet A fuel were passed through each filter in order to determine physical and/or chemical changes that might occur within the filter due to contact with a liquid hydrocarbon fuel. The filters were again rinsed with isooctane, dried, and reweighed five times. This procedure was repeated with certain filters.

The average isooctane-rinsed filter weight (including Gooch crucible for the glass fiber filters) and weight change after filtration of the Jet A fuel (including a final isooctane-rinse and drying) are shown in Table 5. The standard deviation for the replicate weighings of the isooctane-rinsed filters is also included in Table 5.

For the ester filters, the procedure was to use top and bottom filters sandwiched in the filtration apparatus (same as used in ASTM D 2276, Particulate

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Contaminant in Aviation Turbine Fuels; Laboratory Filtration Method); the data in Table 5 are for the top filter only. When the mixed cellulose ester

TABLE 5. WEIGHING REPEATABILITY OF ISOOCTANE-WASHED FILTERS
BEFORE AND AFTER FILTERING JET A FUEL

Filter Type	Pore Size, μm	Average Weight,*g (Std Deviation, mg)	Average Weight Change After Jet A Fuel Filtration, mg
Glass Fiber (GF/F)	0.7	16.7340 (<0.1)	+0.1
Glass Fiber (GF/C)	1.2	17.5486 (<0.1)	+0.1
Glass Fiber (934AH)	1.5	17.1026 (<0.1)	+0.2
Mixed Cellulose Ester	0.45	0.1849 (<0.1)	−0.6
Mixed Cellulose Ester	0.80	0.1597 (<0.1)	−2.1
Mixed Cellulose Ester	1.2	0.1537 (<0.1)	+0.1

* Weights for glass fiber filters include Gooch crucible weights. The 0.7- and 1.2-μm data were for 10 filters each. The 1.5-μm data were for 15 filters. The mixed cellulose ester data were for five filters for each screen size.

filter pairs were rinsed after filtration, it visually appeared that some fuel remained in the space between the filters. Additional isooctane rinsings of individual filters further reduced the filter weight, thus indicating that a fuel residue did remain in the space between the filters or around the filter edge.

The glass fiber filters contained no binders or fluorescent material, while the cellulose filters contained <5 percent of a Triton wetting agent. The minimal, but consistent, positive weight change for the glass fiber filters (in Table 5) is not much greater than the expected normal deviation from the mean. It is possible that a trace quantity of fuel could have remained after the final isooctane rinse.

The weight loss noted for two of the three cellulose ester filters (a maximum loss of 1.3 percent for the 0.8-μm pore size filter) could be due to solubility of the wetting agent present on the filter surface. The lack of consistency in the final result could reflect an inconsistency in the application of wetting agent to the filter surface. If a reference (bottom filter) were to be used for weight loss correction (assuming equal weight loss of both filters), final D 2276 type values would not be affected by the weight loss phenomenon noted in single filters.

Overall, the consistency of the glass fiber filter tests makes gravimetric analysis appear to be a negligible factor in causing variation in particulate determinations. Use of the cellulose ester filters for further work would appear to potentially lead to a much greater variation in final D 2274 results, unless the use of weight changes in the second filter can be shown to correct for weight changes in the first (top) filter. The precision of gum beaker weighing also needs to be addressed. The variability in beaker weight should be greater than that for the filters and filter holders since the beakers weigh much more and thus would be more subject to environmental humidity, thermal and electrostatic effects.

2. Filter Efficiency

Fifteen filters of varying pore size and/or composition were selected. A description of these filters is given in Table 6. In two separate experiments, approximately 15 or 30 mg (measured to 0.1 mg) of Air Cleaner test dust (Package No. 1543094, Batch No. 114) were weighed and stirred into 1 liter of prefiltered Jet A fuel. Maximum particle size was 176-μm diameter, while 38 ± 3 wt% was less than 5.5-μm diameter. Particles in 38 ± 3 wt% of <5.5-μm diameter had the following distribution:

< 1.0 μm	32.8%
1.0 – 1.65 μm	33.6%
1.65 – 2.7 μm	33.6%
2.7 – 5.5 μm	<0.1%

Fuel mixture aliquots of 100 mL were then filtered. Calculated recoveries of 15 to over 100 percent suggested that the homogeneity of the stock suspension was not adequate to allow the use of an aliquot procedure.

TABLE 6. COMPOSITION AND PORE SIZE OF TEST FILTERS*

Filter Composition	Filter Pore Size, μm
Mixed cellulose ester	0.45, 0.8, 1.2
Glass fiber	0.7, 1.2, 1.5
Composite fiber	0.65
Polytetrafluoroethylene (PTFE)	0.5, 1.0
Nylon	0.45, 1.2

*The effective filtration diameter for all filters was 35 mm.

Solubility of the AC fine dust was checked with isooctane and found to be negligible. Using a more direct approach, 1.5-, 5.25-, and 7.5-mg A/C fine dust were weighed into 100, 350, and 500 mL of filtered Jet A, respectively, in duplicate. The entire fuel volume was then passed through the filters, including multiple rinsings of the flasks with isooctane. These data are summarized in Table 7.

The mixed cellulose ester (MCE) filters are more retentive (efficient) than glass fiber filters of the same general porosity. The 0.45-μm cellulose filter from the primary supplier offered the best percentage of retention (the particulate concentration in the fuel was also a factor of 10 higher than for the other filter tests) and was the only filter to exhibit greater than 90-percent retention of the A/C Fine Dust. Of the remaining four cellulose ester filters, three exhibited better than 80-percent retention while the glass fiber filters exhibited 66- to 76-percent retention. This difference in retention is in agreement with earlier work in this laboratory, which also indicated that the cellulose ester screen filters were generally more retentive than their glass fiber counterparts.[38] While it is generally thought that the efficiency of a filter increases with increasing sample volume, the data in Table 7 does not support this conjecture since no trend to higher percent retention values are observed for filtering of fuel volumes of 100, 350, and 500 mL.

The polytetrafluoroethylene (PTFE) and nylon filters exhibited extreme curling even after drying at a lower temperature of 80°C in preparation for filtration. This curling made them unusable unless extreme care was exercised in their handling.

To more closely approximate filterable particulate formation, commercially available asphaltene resin was dispersed in the Jet A fuel by sonication in a bath. The same weights and filtration volumes were used as with the A/C fine dust. After attempting to disperse the resin, it was found that it was partially soluble in the fuel and that it would not be possible to make a quantitative material balance. Therefore, no further work was performed using the resin materials.

TABLE 7. FILTER EFFICIENCY USING A/C FINE DUST

Filter type	Pore size, μm	Fuel volume, mL A/C FD wt, mg	Average percent retention	Overall average, %
Mixed Cellulose Ester (MCE)	0.45	100/15.0	87	
		350/52.5	97	92
		500/75.0	91	
MCE	0.8	100/1.5	67	
		350/5.2	87	80
		500/7.5	85	
MCE	1.2	100/1.5	80	
		350/5.2	85	82
		500/7.5	80	
MCE(alternate source)	0.45*	100/1.5	70	
		350/5.2	78	74
		500/7.5	73	
MCE(alternate source)	1.2	100/1.5	87	
		350/5.2	86	84
		500/7.5	80	
Glass Fiber GF/F	0.7	100/1.5	73	
		350/5.2	77	76
		500/7.5	79	
Glass Fiber GF/C	1.2	100/1.5	60	
		350/5.2	79	66
		500/7.5	59	
Glass Fiber 934AH	1.5	100/1.5	73	
		350/5.2	71	73
		500/7.5	76	
Composite fiber	0.65	100/1.5	77	
		350/5.2	79	73
		500/7.5	64	

* Slight curl after drying.

3. Effect of No Prefiltration of Test Fuel

In order to determine possible enhanced reactivity due to existing particulates in the fuel, three separate aliquots were obtained from a volume of fuel taken directly from the main storage tanks. To assure homogeneity, the can containing the fuel sample was shaken prior to removal of each aloquot. Of the three aliquots, one was used to determine the existing quantity of insoluble particulate present using ASTM D 2276, "Particulate Contaminant in Aviation Turbine Fuels." A D 2274 procedure was then carried out, in duplicate, using the second aliquot. The third aliquot was used for a modified (no prefiltration) D 2274 procedure (in duplicate).

All four test fuels were analyzed in this manner. The difference between the D 2274 result (fuel not prefiltered) and the D 2276 result was then compared to the D 2274 results obtained through standard test procedures. These results are shown in Table 8. The average deviation between these two results for each fuel is 0.27 mg/100 mL, or approximately 11 percent of the standard D 2274 value.

The D 2276 procedure (0.8-μm filter) would indicate a greater quantity of material to be present in the test fuel than would filtration through the standard 934 AH filter ($\sim$1.5 μm) used in D 2274. This would cause the difference value, indicated in Table 8, to be smaller than it should be for direct data comparison with standard D 2274 results. In three of the four cases, this is shown to be true. Therefore, it does not appear to make a significant difference whether particulate matter remains in the fuel or is removed prior to the experiment as long as proper weight correction is made. It would seem unrealistic to remove (prior to aging tests) particulate that acts either as a catalyst or as a stabilizer when the aging test results could be simply corrected for initial particulate content. If initial particulates are dissolved at the higher aging temperatures and not reformed during cool-down prior to filtration, over correction of final test result values could occur and be perhaps misleading.

The particulate-size/number distribution for the unfiltered test fuels is provided in Appendix B-1.

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TABLE 8. EFFECT OF NO PREFILTRATION OF THE TEST FUEL

Fuel	D 2274 Not Prefiltered			D 2276(B)*	Difference(T-B)	D 2274 Prefiltered		
	P**	A***	T[+]			P	A	T
Cat 1-H	4.90	3.36	8.26	0.49	7.77	4.97	2.51	7.48
DF-2	2.66	0.59	3.25	0.64	2.65	2.49	0.80	3.29
1% S	3.32	0.51	3.83	1.36	2.53	1.8	0.84	2.64
LCO Blend	3.87	0.56	4.43	1.61	2.87	2.49	0.93	3.42

Results, mg/100 mL

* 0.8 μm pore size mixed cellulose ester filter.
** P = filterable insolubles.
*** A = adherent insolubles.
+ T = total insolubles.

C. Phase III: Evaluation of Aging Procedures

The effects of test fuel and tube volume, gas flow on fuel temperature strat-
ification, aging time/temperature, and gas composition/bubbling rate were
evaluated as aging parameters which can cause variation in measurements.

1. Effect of Volume

The effects of fuel and container (test tube) volume variations on the final
D 2274 results were studied using both fixed volumes and volumes required to
maintain a fuel height equivalent to that in a standard oxidation tube (350
mL). Special tubes were fabricated to hold larger test fuel volumes. Details
are given in Figure 1 for two enlarged oxidation test tubes, while the stan-
dard 350-mL oxidation tube is described in D 2274-80.

The special oxidation test tubes, when received, were not made to SwRI design
specifications. For this reason, two related studies were performed. The
first was to place 350, 525, and 750 mL of Cat 1-H in the appropriate tubes
and carry out the aging and analysis in a conventional manner. The second
was to fill each tube to a height equivalent to that of 350 mL in a standard
oxidation tube; this required fuel volumes of 630 mL rather than 525 mL, and
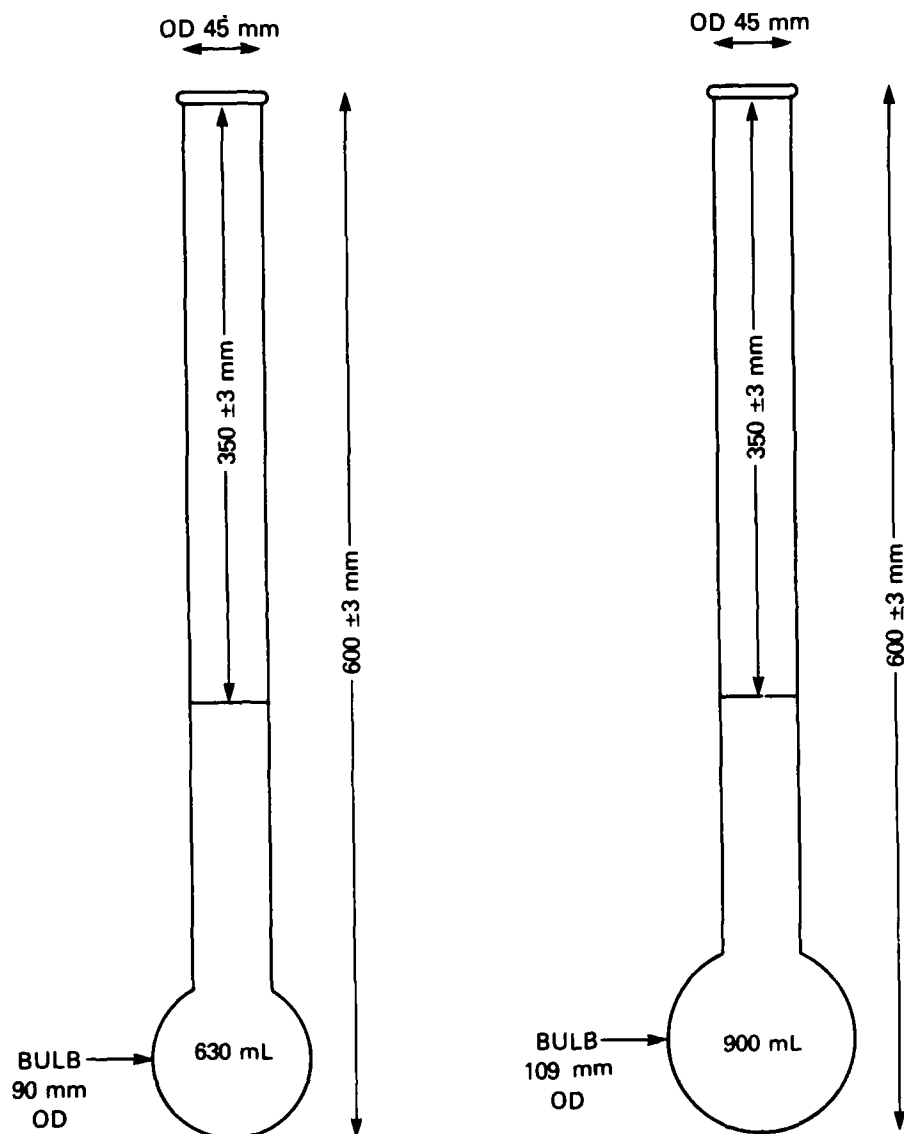
32

FIGURE 1.   OXIDATION TUBES FOR LARGER TEST FUEL VOLUMES

900 mL rather than 750 mL. The results of these tests are summarized in Table 9. These five sets of data, taken as a whole, appear to fall within expected experimental error (repeatability >0.42 mg/100 mL according to ASTM D 2276) indicating that the effect of volume or height in a tube is a negligible contribution to any variation in the D 2274 results. Therefore, any subset trends are considered coincidental. The average value for all five test conditions (in triplicate) was 7.55 mg/100 mL with a data span of ± 12 percent and a standard deviation of ± 6 percent (0.46 mg/100 mL).

Since the evaluation was limited to one fuel at the D 2274 value level of 7.5 mg/100 mL, these experimental results cannot be extrapolated to more stable fuels (e.g., 1 to 1.5 mg/100 mL) or to fuels refined by different processes. A larger data base needs to be developed.

2. Effect of Gas Flow on Fuel Temperature

In this experiment, three thermocouples were fastened to the bubbler tube such that the ends would be halfway between the outside of the bubbler tube and the inner surface of the oxidation test tube. Vertical placement was at

TABLE 9. EFFECT OF VARIOUS FUEL VOLUMES/HEIGHTS ON
D 2274 TEST RESULTS FOR CAT 1-H

Volume, mL	Result, mg/100 mL		
	Particulates	Adherents	Total
350*	4.97	2.51	7.48
525	5.38	1.19	6.57
	4.29	3.53	7.82
630*	5.47	1.38	6.85
750	2.99	3.34	6.33
	5.22	3.01	8.23
900*	5.22	2.10	7.32
Average ± std deviation = 7.55 ± 0.46 (6%)			

*Equivalent fluid column height in tube.

25, 50, and 75 percent of the fuel height. Temperatures were recorded from a digital meter after submersion of the test tube in the 95°C heating bath for 30 minutes. Readings were then taken every 10 minutes for a period of 2 hours. Data were obtained using the Standard D 2274 test tube both with and without bubbling.

Under conditions of no gas flow, there was a temperature stratification of approximately 3° to 5°C over the length of the tube. No obvious cooling or heating differences were noted due to oxygen flow through the fuel at 3 liters/hr (the standard D 2274 condition). Mixing due to gas flow was effective, thus maintaining the desired 95°C temperature throughout the tube after the initial 30-minute delay for equilibrium to be reached.

3. Time/Temperature Effects

The LCO Blend and Cat 1-H fuels were subjected to a time/temperature matrix consisting of multiple samples aged at 80°C (175°F) for 16 hours, 95°C (203°F) for 8, 16, and 24 hours; and 108°C (225°F) for 16 hours. Filtration techniques, volume, gas flow, and other parameters were as specified in the D 2274 procedure. These data are summarized in Table 10, which includes both multiple and average D 2274 test results.

Figure 2 shows the total insolubles formed as a function of time for both the LCO Blend and Cat 1-H fuels. The line plotted for each set of data indicates the assumed values for linear extrapolation of the D 2274 result (16 hrs,

TABLE 10. EFFECT OF TIME/TEMPERATURE VARIATIONS

Time, Hours	Temp, °C(°F)	Ratio of Particulates to Adherents (by weight)		Average D 2274 Results (Actual), mg/100 mL	
		Cat 1-H	Cat Cracked	Cat 1-H	LCO Blend
8	95(203)	3:1	10:1	2.38(2.71,2.85,2.34, 2.17,2.13,1.97)	3.32(3.30,3.33,3.33)
16	95(203)	2:1	3:1	7.49(6.83,7.49,7.03, 8.09,7.54,7.94)	3.46(3.39,3.54,3.45)
24	95(203)	1.5:1	10:1	11.02(10.38,10.81,13.80) 10.75,10.08,11.22)	10.34(10.23,10.35,10.43)
16	80(175)	1:1	2:1	0.29(0.32,0.29,0.29, 0.29,0.10,0.32)	1.34(1.28,1.33,1.42)
16	108(225)	1:1	10:1	22.74(19.42,24.55,22.99, 22.75,22.99,23.74)	12.7 (12.8,12.7,12.7)
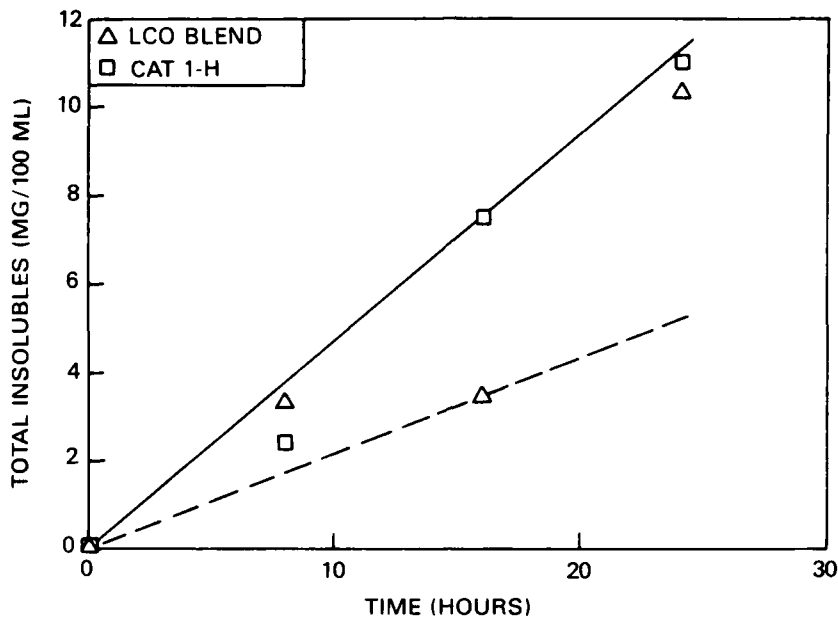
FIGURE 2.   EFFECT OF TIME ON TOTAL INSOLUBLE FORMATION AT 95°C

95°C) through zero time. One can readily see for LCO Blend fuel that the
data do not agree with the assumption. For the Cat 1-H fuel, there appears
to be a better fit to linearity; however, one data point (at 8 hours) still
indicates that the assumption is not valid. Although a larger data base is
required, it can be seen that an arbitrary choice of a single time and tem-
perature can not adequately describe the insoluble product formation at other
test times at that temperature.

Figure 3 shows the Arrhenius plot which has been assumed to show linear
extrapolation to all working temperatures (including ambient storage). One
can again see from this limited data that a linear plot does not necessarily
result and that the original assumption can be in error.
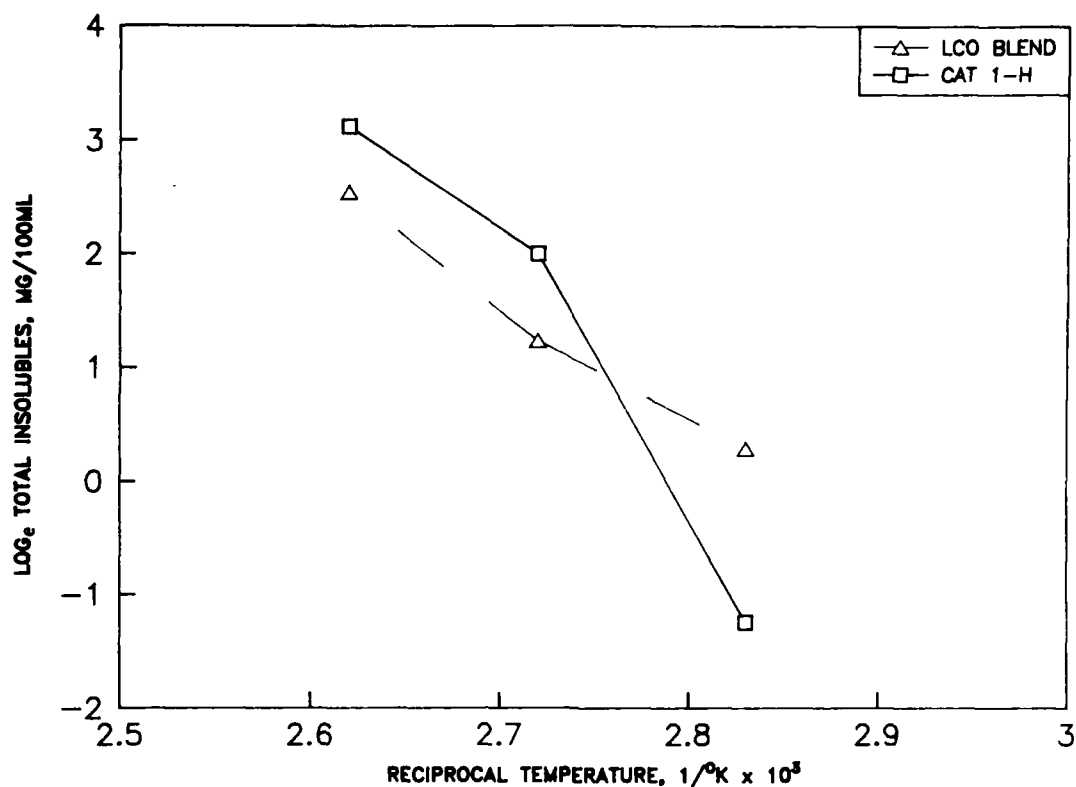
FIGURE 3. EFFECT OF TEMPERATURE ON INSOLUBLE FORMATION AT 16 HOURS

Since neither fuel yielded a linear Arrhenius plot, it is possible that the products generated at the three temperatures were not formed from the same reaction sequences. Should this be the case, then a much more in-depth study should be made to determine the maximum temperature that can be used for accelerated aging processes and still be a true predictor of ambient storage stability. This type of evaluation would also greatly benefit if additional data, such as peroxide number, radicals by electron spin resonance (ESR), and nephelometer data were also simultaneously developed.

The ratio of particulates to adherents ranged from 1:1 to 3:1 (Table 10) for Cat 1-H whereas they ranged from 2:1 to 10:1 for LCO Blend fuel. Note the higher 10:1 ratio was consistent at both 24 hours (95°C) and 16 hours (108°C) with the lower ratio of 2 to 3:1 at 16 hours (95°C) and 16 hours (80°C).

Particle counts for Cat 1-H and the LCO Blend fuel at 16 hours (80°, 95°, and 108°C) are provided in Appendix B.

4. Effect of Gas Composition and Bubbling Rate

Oxygen (O_2), air, and nitrogen (N_2) flowing at 3 ± 0.3 liters/hr and air at atmospheric pressure (no flow) for 16 hours were used to determine the effect of gas composition on D 2274 results for the Cat 1-H and LCO Blend test fuels. Other than these changes, standard D 2274 techniques were employed.

A substantial increase in total insolubles resulted for the Cat 1-H when oxygen was bubbled through the system. In the other three cases, the LCO Blend fuel yielded the highest total insoluble weights based on Table 11 and Figure 4. Particle size distribution data are provided for these tests in Appendix B.

TABLE 11. EFFECTS OF OXYGEN, AIR, NITROGEN, AND
NO BUBBLING ON D 2274 RESULTS

Fuel	Total Insolubles by D 2274, mg/mL			
	Oxygen	Air	Nitrogen	Air, No Bubbling
Cat 1-H	7.49	1.34	0.28	0.99
LCO Blend	3.46	3.94	1.05	2.30

The positive D 2274 result obtained even though an inert gas (N_2) was used to purge the fuel system indicates that other secondary physical or chemical reactions besides the oxidation reaction (with dissolved oxygen) are contributing to the total insolubles formation assuming assurance that oxygen was completely absent. The cause of these other reactions and a method to predict their contribution to the magnitude of the final accelerated oxidation test result would probably have a significant effect in moderating the current variability of these results. The effect of loss of reactive hydrocarbon material due to purging of the test tube with gas did not lend itself to an evaluation using these test conditions.
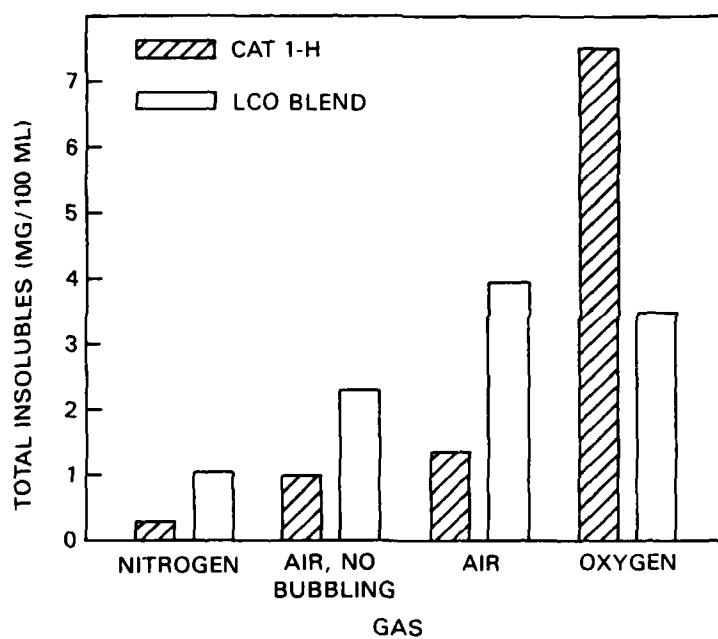
FIGURE 4. EFFECT OF TYPE OF GAS FLOW ON TOTAL INSOLUBLES
FOR CAT 1-H AND LCO Blend FUELS

D. __Phase IV__: Ev   ᵤᵢion of Post-Aging Procedures

Determination of adherent gum solvent evaporation rate, solvent effectiveness
in removing wall adherent gum, comparison of air jet versus hot plate gum
solvent removal, and the effects of cool-down temperature/times were identi-
fied as post-aging procedure for evaluation.

1. __Determination of Adherent Gum Solvent Evaporation Rate (Hot Plate__
   __Method)__

Evaporation of adherent gum solvent (equal volumes of toluene, acetone, and
methanol, TAM) has normally been accomplished using a standard air jet evapo-
ration (ASTM D 381) apparatus. This apparatus is not available in many
laboratories; therefore, an alternative procedure has been suggested and
applied. This procedure involves normal evaporation of the solvent from a
beaker placed on a thermostated hotplate. The criterium set for this alter-
native process was that dryness should be reached in approximately 30 minutes
or less.

For this evaluation, two 100-mL "tall" beakers containing 75 mL of TAM and
THF (tetrahydrofuran), a possible alternative solvent, were placed on a tem-
perature-controlled hot plate. An extra beaker containing Teresstic 32 oil
(a high flashpoint (385°F), stable hydrocarbon manufactured by Exxon,
Houston, TX) was also placed on the hot plate. A thermometer was then placed
in this extra beaker (bulb on bottom) to monitor the temperature, which was
varied for several different evaporation attempts until the beakers dried in
approximately 30 minutes.

Evaporation of the TAM and THF solvents within the 30-minute time period was
accomplished with some difficulty because of bumping/splashing and solvent
condensation on the beaker wall. These problems were eliminated by employing
a flow of dry N_2 over the surface of the liquid. It was determined that a
hot-plate temperature of 130°-135°C was required to obtain a drying time of
approximately 30 minutes. These data are shown in Table 12.

TABLE 12. EVAPORATION TIMES/TEMPERATURES

Solvent	Temperature Range, °C (°F)	Heating Time, min	Residue, mg
TAM (75 mL)	95–98 (203–208)	65	0.7, 0.3
	110–114 (230–237)	120	<0.1
	120–123 (248–253)	60	0.1
	130–135 (266–275)	35[a]	<0.1
	130–135 (266–275)[b]	35[c]	0.8
	130–135 (266–275)[d]	20	0.8
THF (75 mL)	130–135 (266–275)[b]	20[e]	2.4, 3.3
	130–135 (266–275)[d]	Until Dry	0.4

a) bumping occurred
b) boiling beads used
c) minor bump
d) N_2 surface flow
e) sides of beaker still wet after 50 minutes

Even though the time periods required to evaporate the solvent are short compared to the original aging time, the temperatures used are significantly higher than the original aging temperature. This could lead to additional insolubles weight through further residue oxidation. Lower temperature methods should be studied (e.g., at reduced pressure) to determine if this is, in fact, what is happening.

2. Solvent Effectiveness for Adherent Gum Removal

Total removal of wall adherent fuel insoluble material from the reaction tube is quantitatively desirable. Occasionally after a TAM wash, a brown film is still observable on the tube walls.

Two solvents, THF and DMF (dimethylformamide), were used to evaluate the solvent effectiveness of TAM for adherent gum removal. Adherent gums formed from standard D 2274 aging of Cat 1-H fuel were rinsed with TAM followed by either THF or DMF, the data for which are shown in Table 13. Initial solvent evaporation was by hot plate, followed by a final drying with the air jet

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assembly (ASTM D 381). The difference between initial hot plate data and final air jet data was considered as a measure of the drying efficiency.

The twelve D 2274 tests in Table 13 were conducted in sets of two so that one tube was retained for adherent gum removal after overnight storage. In each case, there was an apparent weight gain of approximately 7 mg on the average in adherent gums when left in the tubes overnight and then removed to beakers the next day. The THF weights in Table 13 are significantly lower after air jet drying, indicating inefficient drying (THF evaporation) by the hot plate method. The TAM and DMF weights were fairly consistent using the air jet method as compared to the hot plate method. Under the same conditions of evaporation, the solvent blanks yielded no measurable residue. On the average, both the THF and DMF used as a final wash appeared to remove an additional 5 to 10 percent of the TAM soluble gum value from the test tube.

TABLE 13. COMPARISON OF SOLVENT AND TIME EFFECTS ON
ADHERENT GUM WEIGHTS

| Adherent Gum Weights Measured Immediately, mg/100 mL | | | | | | Adherent Gum Weights Measured After Approx. 22 hr, mg/100 mL | | | | | |
| Hot Plate* | | | Air Jet | | | Hot Plate* | | | Air Jet | | |
TAM	THF	DMF	TAM	THF	DMF	TAM	THF	DMF	TAM	THF	DMF
4.8	2.3		4.8	0.8		14.4	2.2		13.2	0.4	
3.6	2.9		3.2	0.6		14.4	3.3		12.9	0.3	
5.5	6.5		4.8	0.0		8.5	4.2		8.2	1.6	
5.2	6.3		4.7	2.2		12.8	4.2		12.4	1.9	
5.1		0.4	5.4		0.4	12.5		–	11.4		–
4.6		0.4	4.8		0.5	10.3		1.0	8.9		0.0

*Hot plate temperature maintained at 135°C.

To further evaluate the effects of TAM and DMF (but not THF due to inefficient drying by hot plate) as wall adherent gum solvents in the D 2274 procedure, they were investigated concurrently using Cat 1-H fuel. The data obtained are summarized in Table 14 using both the hot plate and the air jet methods for solvent evaporation. The data point indicating 2.2 mg/100 mL adherent insolubles could be considered an outlier; however, since it is accompanied by an elevated particulate weight, this may also indicate a variation in insolubles formation. With both hot plate and air jet evapora-

TABLE 14. SOLVENT EFFECTS AND HOT PLATE
VERSUS AIR JET DRYING METHODS IN D 2274 RESULTS

Method	Temp, °C(°F)	Solvent	Particulate Weight, mg/100 mL	Adherent Weight, mg/100 mL	Total Weight, mg/100 mL
Hot plate	135(275)	TAM	3.9	4.7	8.6
			3.1	4.4	7.5
			4.5	4.4	8.9
	172(342)	DMF	4.9	6.4	11.3
			4.6	5.0	9.6
			5.3	2.2	7.5
Air Jet	150(302)	TAM	3.1	3.9	7.0
			3.0	3.7	6.7
			3.2	4.1	7.3
	150(302)	DMF	3.2	4.5	7.3
			3.1	4.0	7.1
			4.5	4.6	9.1

tive techniques, the TAM solvent appeared to yield less erratic results while
the DMF yielded directionally higher adherent weight results, in particular
for the air jet method. These data suggest that (for this one fuel), DMF is
a better solvent for wall adherent insolubles in the D 2274 procedure.

3. Effect of Cool-Down Times/Temperatures

The post-aging cool-down procedure was studied using three different tempera-
tures and three different times for each temperature. Upon removal from the
oil bath, the reaction tube was immediately placed in an environment with a
temperature of 0°C, room temperature (~25°C) or 35° to 40°C for 2, 4 or 6
hours: a total of nine different test conditions.

In this evaluation, Cat 1-H was studied to a greater extent than were the
other fuels because of its tendency to form a greater quantity of fuel insol-
uble deterioration products. Indications are that more insoluble material is
formed at room temperature (~25°C) than at 0°C for the 2- and 4-hour periods
(Table 15). At 6 hours, the 0°C and room temperature results are comparable.

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TABLE 15. EFFECT OF VARIABLE COOL-DOWN TIMES
AND TEMPERATURES ON D 2274 RESULTS

Cool-down Time, Hr	Fuel	D 2274 Results at Final Temperature, mg/100 mL* 0°C			Room			35+°C		
		Part.	Adh.	Total	Part.	Adh.	Total	Part.	Adh.	Total
2	Cat 1-H	6.55	1.49	8.04	3.65	3.81	7.46	5.07	1.23	6.30
	LCO Blend				2.55	0.77	3.32			
	1% S				1.45	0.77	2.22			
	DF-2				2.34	0.66	3.00			
4	Cat 1-H	2.46	0.86	3.32	3.97	3.11	7.08	5.24	1.24	6.48
	LCO Blend				2.49	0.93	3.42			
	1% S	2.53	0.74	3.27	1.83	0.74	2.57			
	DF-2				2.70	0.57	3.27			
6	Cat 1-H	5.59	1.08	6.67	5.07	1.67	6.74			

*Note: Part. - Filterable Insolubles
Adh. - Adherent Insolubles

Since these data represent single determinations, the 3.32 value (in Table 15) for Cat 1-H when cooled-down for 4 hours at 0°C, is considered an outlier. There also appears to be a slight decrease of total insolubles at 35+°C. Since accurate control at 35°C was not obtained, the temperature actually ranged from 35° to 40°C.

E.   Phase V: Application of Program Results

A revised accelerated aging procedure and round-robin testing program were created to determine if an improvement in repeatability and reproducibility could be obtained compared to the existing ASTM D 2274 method.

1.   A New Procedure

An initial modification to the original ASTM D 2274 procedure was formulated by Dr. Edmund White (DTNSRDC). These modifications were based on discussions at the first Task Force meeting held in 1983 at Annapolis, MD. A second revision was formulated based on some of the results discussed in this report and results of a similar program conducted by E.W. White (37). This revised method was reviewed and commented on by the ASTM task force and then finalized for round-robin test evaluation. This test method is provided as Appendix C. Major differences between this method and the ASTM D 2274 method are:

a.   Filtration using cellulose ester screen filters rather than glass fiber filters.

b.   Use of separatory funnel in prefiltration eliminated.

c.   Adherent gum can be determined by a hot plate drying method or the standard air jet method.

2.   A Round-Robin Test

Those laboratories that had earlier shown an interest in participating in a round-robin test program were contacted to determine the extent to which a round-robin program to evaluate the revised accelerated oxidation procedure might be conducted. In cooperation with the ASTM D-2 (on Petroleum and Petroleum Products) task force formed under the jurisdiction of D02.0E.05 and D02.09.0B, six fuels were chosen for cooperative testing:

Fuel No. 1:   Gas oil (from the United Kingdom)

Fuel No. 2:   D-2 Reference Diesel Fuel

Fuel No. 3:   Clay-treated unstable F-76 (Naval Distillate Fuel) (MIL-F-16884H)

Fuel No. 4:   Caterpillar 1-H/1-G engine test reference fuel

Fuel No. 5:   F-76 (Naval Distillate Fuel) (MIL-F-16884H)

Fuel No. 6:   No. 2 heating oil, ASTM D 396.

Each fuel (approximately 1800 mL) was placed in a 2-liter can, and the ullage was filled with argon. The cans and pertinent test information were placed in wooden crates and shipped by air freight to each of the participating laboratories.

A total of 17 laboratories from five countries participated in the round-robin test. Each laboratory analyzed six fuels by either hot plate, air jet, or both methods. Fuel analysis sequence for both the air jet and the hot plate method was: Fuel No. 1 through Fuel No. 6 followed by a repeat of Fuel No. 1. Separate sets of sample cans for fuel No. 1 were provided for each of the methods. A summary of the data, based on all (statistically) acceptable data from all laboratories, is provided in Table 16. Because of statistical rejection of either filterable particulate, adherent, or total insoluble data, the sum of average filterable particulates and average adherents will not necessarily equal the average total insolubles. This is particularly true of data for fuel No. 1 in Table 16.

Overall, the values obtained using the hot plate evaporation technique tend to be higher than those using the air jet method.

The high viscosity of Fuel No. 1 caused great difficulty in several laboratories and, as a result, also appeared to cause a wide range of results to be reported for Fuel No. 1. The higher values reported for hot plate evaporation to determine adherent insolubles (compared to the air jet method) in Samples 2 through 6 are consistent with the earlier findings in this report for other fuels. Not explainable at this time is the reasons that the particulate values in Table 16 are constantly higher for the hot plate method (versus air jet method) since the method of solvent evaporation has no bearing on this portion of the stability test. It is possible that laboratory bias may play a role in this since some of the laboratories using the hot plate method did not contribute to the air jet portion of the evaluation protocol, and vice versa. Further analysis of the raw data will be required for this to be verified.

TABLE 16. AVERAGE FINAL TEST RESULTS (mg/100 mL)

| Fuel No. | Method* | Insolubles, mg/100 mL | | |
		Filterable Particules	Adherents	Total Insolubles
1	A	0.37	0.59	1.27
	A**	0.23	0.47	0.77
	A	[0.30]+	[0.53]	[0.98]
	H	0.39	0.49	0.70
	H**	0.44	0.36	1.08
	H	[0.42]	[0.42]	[0.92]
2	A	0.05	0.17	0.21
	H	0.06	0.25	0.30
3	A	0.72	0.31	1.03
	H	0.77	0.46	1.22
4	A	0.68	0.33	1.06
	H	0.90	0.37	1.31
5	A	2.09	0.53	2.57
	H	2.23	0.61	2.83
6	A	0.07	0.26	0.33
	H	0.12	0.28	0.40

* A = Air Jet Method; H = Hot Plate Method
**Repeat of Sample 1 after finishing samples 2 through 6.
+ [Average Value]

The repeatability and reproducibility data provided in Table 17 are based on a statistical analysis of all the data obtained for fuel sample Nos. 1 through 6. While these values show a statistical advantage for the hot plate procedure over that of the air jet procedure, they are not appreciably better than that of the D 2274 method. Table 18 provides the calculated repeatability and reproducibility data based on results for Test Fuel Nos. 2 through 6 (eliminating Test Fuel No. 1). These data show a significant advantage in the air jet method over the hot plate method, both for adherents and overall total insolubles. The accelerated test method utilizing the air jet procedure gave repeatability and reproducibility values of 0.36 and 0.83, respectively, for the range of 0.21-2.57 mg/100 mL (Table 18) representing a significant improvement in this method over that of D 2274.

TABLE 17. REPEATABILITY AND REPRODUCIBILITY DATA BASED
ON FUEL SAMPLES 1 THROUGH 6
(No Transformation)

Test	Repeatability	Reproducibility	Range of Round-Robin Test Results, mg/100 mL
Hot Plate Procedure			
Filterable Particulates	0.29	0.64	0.06-2.23
Adherents	0.34	0.81	0.25-0.61
Total Insolubles	0.35	1.15	0.3-2.83
Air Jet Procedure			
Filterable Particulates	0.25	0.54	0.05-2.09
Adherents	0.25	0.99	0.17-0.53
Total Insolubles	0.79	1.83	0.21-2.57

TABLE 18. REPEATABILITY AND REPRODUCIBILITY DATA BASED
ON FUEL SAMPLES 2 THROUGH 6
(No Transformation)

Test	Repeatability	Reproducibility	Range of Round-Robin Test Results, mg/100 mL
Hot Plate Procedure			
Filterable Particulates	0.28	0.82	0.06-2.23
Adherents	0.36	0.77	0.25-0.61
Total Insolubles	0.37	1.22	0.3-2.83
Air Jet Procedure			
Filterable Particulates	0.31	0.60	0.05-2.09
Adherents	0.22	0.52	0.17-0.53
Total Insolubles	0.36	0.83	0.21-2.57

Table 19 is a summary of results of the statistical analysis of round-robin data for the years 1964, 1972, 1978, and 1985. The data for 1972 were recalculated upon finding an error in the original calculation. There appears to be some real improvement over time in both repeatability and reproducibility using the 1985 statistical analysis values.

TABLE 19. STATISTICAL ANALYSIS

Total Insoluble Level, mg/100 mL	1964		1972	1978		1985	
	<1	>1	1-5	<1	>1	0-5**	
						Air Jet	Hot Plate
Repeatability	0.41	0.85	1.3*	0.3	0.9	$0.54TI^{0.25}$	$0.42TI^{0.25}$
Reproducibility	1.2	3.4	2.4*	1.0	3.0	$1.06TI^{0.25}$	$1.28TI^{0.25}$

*Recalculated.

**$TI^{0.25}$ = Value for total insolubles to the 1/4 power.

Comparison of the round-robin data obtained here and the data reported by Dr. Ed Barry (10) for D 2274 are being further evaluated to determine the viability of this revised accelerated stability method.

Standard D 2274 values were obtained at BFLRF on the round-robin test fuels and are summarized in Table 20. Except for Fuel No. 4, the total insolubles data in Tables 16 and 17 are very comparable. The D 2274 value of 2.53 mg/100 mL is considerably larger than the values of 1.06 and 1.31 mg/100 mL shown in Table 16 for total insolubles by the air jet procedure and the hot plate procedure, respectively. Note that the filterable particulates values of 0.68 and 0.90 mg/100 mL compare very favorably with the filterable particulates values of 0.80 in Table 20.

TABLE 20. STANDARD D 2274 VALUES FOR TEST
FUEL NUMBERS 1 THROUGH 6

Fuel No.	Filterable Particulates	Adherents	Total Insolubles
1	0.46	1.14	1.60
2	0.24	0.00	0.24
3	0.85	0.06	0.91
4	0.80	1.73	2.53
5	2.37	0.76	3.13
6	0.20	0.08	0.28

IV. SUMMARY AND CONCLUSIONS

Prediction of fuel storage stability using accelerated aging conditions has been shown to yield poor precision in the region where insoluble gum formation limits have been established. In an attempt to determine where the major sources of error could occur, 10 of the most commonly used tests were reviewed. A minimum of 16 definable procedural areas (e.g., filtration media, adherent gum solvent efficiency, gum solvent removal method, etc.) were identified and discussed as sources of error. As an error assessment summary, seven general procedural areas were recommended for further study and evaluation in support of developing an improved accelerated stability test method. Based on these recommendations, a laboratory program was initiated to verify these sources of procedural error. This program was divided into three phases involving preaging, aging, and post-aging procedures.

As preaging parameters could procedurally affect test results, weighing repeatability, filter efficiency, and effect of no prefiltration of test fuel were selected for evaluation. The following general observations were made:

1. The gravimetric procedure for filters has a high precision and therefore should not cause significant variations in final test data. Similar results for beaker weight probably would not have the same minimum effect; however, this should be evaluated.

2. Cellulose ester filters containing a hydrocarbon-soluble wetting agent are subject to significant weight loss after filtration and therefore are not acceptable for single filter filtration procedures when small quantities of filterable particulates are generated in aging tests. This weight loss may be overcome by using matched pairs. The use of Triton may affect the results of the weighing procedure and would need to be reevaluated. A great deal of satisfactory experience with matched pair cellulose ester filters applied to jet fuels (using ASTM D 2276) has been developed.

3. Cellulose ester (as opposed to glass fiber) filters are generally more efficient for retaining A/C Fine Test Dust.

4. Use of PTFE and nylon filters is unacceptable unless other drying methods can be found to prevent excessive curling.

5. In the limited matrix of data presented, there appears to be no advantage to prefiltration of the test sample if appropriate correction is made for particulate matter present in the "as received" fuel. This would then allow the particulate to offset synergistically or otherwise the aging test results. There was no opportunity in the experimental matrix employed in this program to determine if contaminant escaping initial filtration significantly contributes to the magnitude of the final aging test result. Most tests of this nature generally require sample prefiltration, especially if large pieces of rust, dirt, or other debris is present. Hence, the question here also becomes one of how "fine" the prefiltration media should be.

The aging parameters which could procedurally affect test results included in this evaluation were: the effects of test fuel and tube volume, gas flow on fuel temperature stratification, aging time/temperature, and purge gas composition. The following observations were made:

1. Use of one time period at one temperature (for example, 16 hr at 95°C as in D 2274) may not give a true indication of a fuel's instability. The limited data suggested that more than one time period should be used, or, perhaps, time to reach a given weight of insolubles (e.g., time to reach 4 mg/100 mL); however, much more extensive data are needed.

2. Within expected repeatability, variation of fuel volume and test tube volume did not appear to affect the quantity of total insolubles formed (expressed as mg/100 mL) in Cat 1-H fuel.

3. Purging the fuel sample during aging tests does not change the temperature of the sample with respect to its surroundings. It does act to mix the sample to obtain a more uniform sample temperature.

4. For Cat 1-H test fuel at temperatures above 80°C, there appears to be a change in particle formation mechanisms.

The post-aging parameters chosen for evaluation as sources of procedural error included the adherent gum solvent evaporation rate, solvent effectiveness in removing wall adherent gum, comparison of air jet versus hot plate gum solvent removal, and the effects of cool-down temperature/times. The following observations were made in this phase of the program.

1. 75 mL of either TAM or THF in "tall" 100-mL beakers could be evaporated in approximately 30 minutes on a hot plate (with the reference fluid maintained at 130°-135°C) by employing a flow of dry nitrogen over the surface of the liquid.

2. In adherent gum determinations for Cat 1-H, TAM was 92+ percent efficiently removed by the hot plate procedure based on residue losses after air jet drying. THF washing of the TAM-washed test tubes contributed an additional residue of approximately 20 percent at the 4.6 mg/100 mL residue level after air jet drying; hot plate drying was not efficient in removing THF from the adherent residue which was estimated to be approximately 80 percent of the 4.5 mg/100 ml residue.

3. Use of DMF, as opposed to TAM, for wall adherent gum removal did not provide as consistent (repeatable) results as did TAM: however, DMF did appear to be a more effective solvent.

4. Storing the test tubes for 22 hours after test fuel removal led to a dramatic increase in the wall adherent residue levels, amounting to an error deviation of approximately 6 mg/100 mL at the 5 mg/ 100 mL adherent insolubles level.

5. Upon cooling of the test fuels after oxidation, quantity of particulate matter formed may be a function of the cooling temperature (to which the oxidation test tube is exposed).

A revised accelerated aging procedure and round-robin testing program were created to determine if better repeatability and reproducibility could be obtained compared to that existing in the ASTM D 2274 method.

Results of the round-robin procedure, while not yet fully evaluated by statistical means, suggest that some improvement in the repeatability and reproducibility has been achieved. No large advantage was demonstrated between the use of a hot plate or the standard air jet evaporation method. Since one of the test fuels was very difficult to filter due to its viscosity, consideration should be given to eliminating data for this fuel from the statistical analysis and placing a viscosity limit on test fuels in the scope of this new method.

Even if the repeatability of this method is shown to be better than that of D 2274, it has yet to be shown that the new method will be a better method for measuring the growing diesel fuel instability tendencies being experienced under user conditions.

V. RECOMMENDATIONS

The following recommendations are made for this project:

1. Evaluate nongravimetric methods for determination of degree of fuel deterioration, e.g., dynamic filtration.

2. Determine if weight loss in cellulose ester filters is correctable using a reference filter and whether cellulose ester filters which do not contain a wetting agent are subject to the same weight variability after filtration as those with wetting agents.

3. Investigate other procedures for using PTFE and nylon filters (which are not subject to fuel solubility) to avoid curling so filter efficiency may also be checked with these filters.

4. Determine if prefiltration through fine pore size filters will assist in making sample preparation more consistent.

5. Perform a sufficiently large matrix of experiments with fuels of varying stability (<1 to >5 mg/100 mL) to determine if larger fuel volumes would yield results with better precision than currently exists. This same fuel matrix should be used to provide an evaluation of wall adherent gum values dependency on tube storage time after test fuel removal.

6. More closely study the potential for particle agglomeration at temperatures above 80°C. Use of scanning electron microscopy equipped with a low-temperature analysis stage may be beneficial for this investigation.

8. The extent and repeatability of the non-O_2 reactions should be determined, particularly with respect to overall contribution to the quantity of fuel insoluble material formed.

9. The accurate determination of adherent gum is hindered by variable solubility in the normally suggested trisolvent system. Therefore, a more comprehensive procedure for quantitative analysis of adherent gum should be determined. More efficient and universally available methods for solvent evaporation should be devised if solvent extraction is continued.

Eventually, a sufficiently large fuel matrix representing various refinery processes and additive treatments must be submitted to testing by an improved test method and a host of storage conditions to establish reliability as a specification criteria.

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APPENDIX A

REQUEST FROM QUADRIPARTITE NAVIES

Canberra.

19 April 1983

Mr P.L. Strigner
Chairman - ASTM Committee D-2
C/- National Research Council
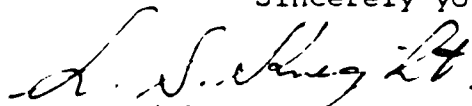OTTAWA   ONTARIO   K1A   OR6
CANADA

Dear Mr Strigner

        We believe that you are aware of the Biennial Fuels
and Lubricants Meetings that are held among the Navies of
the United States, the United Kingdom, Canada, and Australia ...
the so-called Quadripartite Meetings.

        The most recent Quadripartite Meeting was held in
mid-April 1983, in Canberra. During this meeting, all of
the Navies expressed concern about growing Diesel Fuel
instability tendencies. And particular concern was expressed
about the inadequacy of test methods for measuring these
tendencies.

        We need help in this matter, and are writing to you,
as Chairman of ASTM's Committee D-2, to officially request
that considerable emphasis be placed on improvement or
replacement of the D-2274 Accelerated Stability Test Method.
In spite of its demonstrated shortcomings, this test method
is the only short duration method commonly available and
all four Navies must rely on it.

                                Sincerely yours

L.S. Knight,
Delegation Leader, Royal Australian Navy

C.S. Windebank,
Delegation Leader, Royal Navy

R.P. Layne,
Delegation Leader, US Navy

E.E. Lawder, Captain,
Delegation Leader, Canadian Forces

Copy: Chairman I.P. Standardisation Committee

APPENDIX B

PARTICLE DISTRIBUTION

TEST PROCEDURE

"Particle distributions (size and number) were obtained using a HIAC-Royco Model PC 320 with a LAS 346 laser source. The principal of operations was that of single particle light blockage. The particle diameter channels used in this study were 0.5-0.8, 0.8-1.0, 1.0-2.0, 2.0-3.0, 3.0-5.0, and >5.0 μm. To permit a reference to particulate concentrations prior to the start of an aging test, Table B-1 presents "typical" values for these concentrations in one sample fuel (in this case Cat 1-H) and the Jet A dilutent. It will be seen that, except for the last two channels, the test results reported (in later parts of this appendix) are significantly higher than the particulate concentrations found in the unaged fuels.

TABLE B-1. DATA INDICATING APPROXIMATE PARTICULATE
CONCENTRATIONS IN TEST FUEL (Cat 1-H)

	No. Particles/mL					
	Apparent Particle Diameter (μm)					
	0.5-0.8	0.8-1.0	1.0-2.0	2.0-3.0	3.0-5.0	>5.0
Neat Fuel as Received (Unfiltered)	184,780	29,720	16,060	6,900	6,060	1,880
Neat Fuel, (0.8-μm Cellulose Ester Screen Filter)	26,020	5,220	2,860	1,400	900	540
Jet A (diluent) (0.2-μm Cellulose Ester Screen Filter)	273	16	19	5	1	0

Instrument Parameter

The instrument was operated within the parameters listed in the operating manual provided by the manufacturer.

Sample Dilution Procedure

Jet A fuel used as a diluent is prefiltered through a 0.45-μm filter. Iso-octane used to clean cell and lines in instrument and glassware is also prefiltered through a 0.45-μm filter.

All glassware to be used in testing is rinsed in isooctane, then placed in a sonic bath for at least 30 minutes. Glassware is thoroughly rinsed with tap water first, then deionized water. The final rinse is with prefiltered isooctane. Aluminum foil is placed over the tops of glassware to prevent any contamination from airborne particles.

The minimum amount of sample required is 150 mL if sample is not to be diluted. Prefiltered Jet A fuel is used for the first three runs in order to establish a baseline. The sample is then collected in a clean vessel and run through the instrument. Ten mL of the sample is actually read by the instrument and this is done for a total of three runs. The three runs are averaged for the final count.

If the sample is too concentrated, the sensor output lights on the instrument will blink to indicate a dilution is necessary.

Place 150 mL prefiltered Jet A into a clean beaker and add 1.5 mL sample for initial 100:1 dilution. If sample is still too concentrated, further dilutions are required.

To report the counts when the sample is diluted, the following formula is used:

$$(\text{Avg of particle counts} - \text{avg of baseline}) \frac{\text{Dilution factor}}{\text{Volume, mL}} = \text{Particles/mL}$$

Calculated Particulate Concentration

The particle weight per unit volume was calculated from the formula for the volume of a sphere, and an assumed particle density. The form of the equation was

$$W = \sum_{n=1}^{X} N_n \frac{4}{3} \pi R_n^3 D \qquad (B-1)$$

where W is the weight per unit volume of the particles

X is the number of size ranges studied

N_n is the number of particles per unit volume counted in size range n

R_n is the mean radius in size range n

D is the particle density

Six channels were employed with the final apparent particle diameter discrimination selection being 0.5-0.8 μm (Channel 1), 0.8-1.0 μm (Channel 2), 1.0-2.0 μm (Channel 3), 2.0-3.0 μm (Channel 4), 3.0-5.0 μm (Channel 5), and >5 μm (Channel 6).

The particle concentration was calculated using Equation (B-1) in the following form:

$$\text{Concentration (mg/L)} = (0.129\ N_1 + 0.344\ N_2 + 1.590\ N_3 + 7.363\ N_4 + 30.16\ N_5 + 241.274\ N_6) \times 10^{-6} \qquad (B-2)$$

where $N_1 - N_6$ are the number of particles counted in each channel, respectively.

The average of maximum and minimum particle radii detected by each channel was used for R_n. The assumption of 0.9 gm/cm^3 was used for particle density.

Five of the channels used were discretely defined. However, the highest channel, Channel 6 ($\geq$5 μm), is open ended. In these studies, a mean diameter of 8.0 μm was assumed for Channel 6. However, further work is required to determine the validity of this assumption.

These data are reported as calculated weight in mg/L in each of the tables of this appendix.

1. Effect of No Prefiltration on D 2274 Type Filterable Insolubles

Using D 2274 conditions without prefiltration, four test fuels are shown in Table B-2.

TABLE B-2.   FILTERABLE INSOLUBLES BY D 2274 MODIFIED WITHOUT
PREFILTRATION OF SAMPLE

Fuel	Results, mg/100 mL
	P*
Cat 1-H	4.90
DF-2	2.66
1% S	3.32
LCO Blend	3.87

* P = Filterable Insolubles.

Table B-3 reflects the particulate-size/number distribution for the unfiltered test fuels after D 2274 aging. Figure B-1 represents the particle-count distribution before the final filtration (after aging). The increase in concentration of particles in the 1- to 2-μm range for LCO and DF-2 fuels may indicate agglomeration. The effect of this increase in particle size on the value of the final D 2274 result cannot be determined from the current experimental matrix.

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TABLE B-3. PARTICLE COUNTS FOR UNFILTERED FUEL AGED BY D 2274:
BEFORE AND AFTER FINAL FILTRATION
(No. Particles/mL)

Particle Diameter, μm	Cat 1-H			DF-2		
	Before	After	Difference	Before	After	Difference
0.5-0.8	650000	549000	101000	1834000	355000	1479000
0.8-1.0	63100	51600	11500	420000	80000	340000
1.0-2.0	49300	57000	-7700	1011000	373000	638000
2.0-3.0	11000	15200	-4100	281000	153000	128000
3.0-5.0	1300	840	460	15500	1800	13700
>5.0	400	200	200	290	280	10
Calculated wt, mg/L	0.40	0.36		4.59	1.91	

Particle Diameter, μm	1% S			LCO Blend		
	Before	After	Difference	Before	After	Difference
0.5-0.8	4833000	2282000	2551000	1297000	4830000	-3533000
0.8-1.0	198000	15000	183000	676000	1939000	-1263000
1.0-2.0	166000	17100	149000	976000	581000	395000
2.0-3.0	172000	8500	164000	73700	11000	62700
3.0-5.0	570	400	170	1400	1500	-100
>5.0	310	430	-120	110	850	-740
Calculated wt, mg/L	2.31	0.51		2.56	1.94	
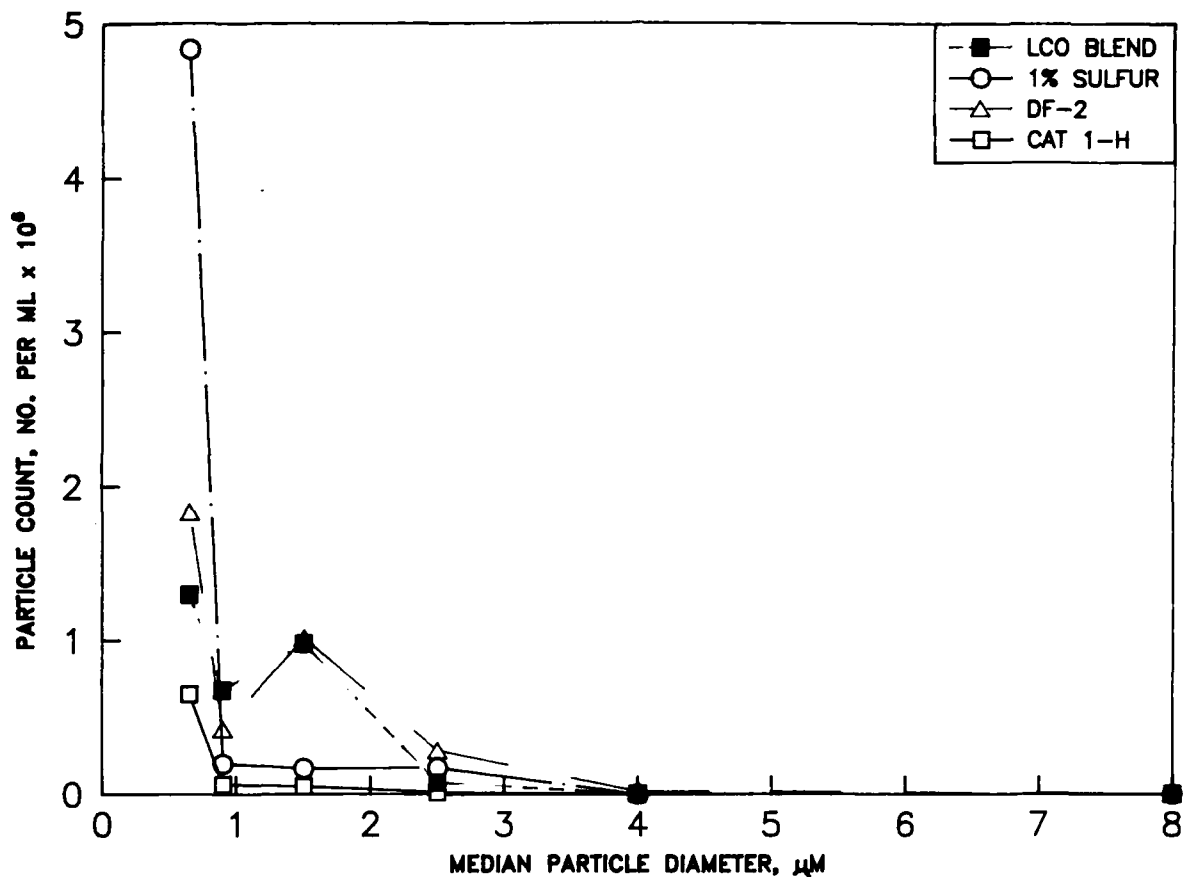
FIGURE B-1.   PARTICLE COUNT FOR UNFILTERED FUELS AFTER
AGING BUT PRIOR TO FINAL FILTRATION

2.   Effect of D 2274 Test Tube Volume

Table B-4 summarizes the particulates by D 2274 for various Cat 1-H test fuel
volumes and heights in the standard and modified D 2274 test tubes.

The average particle-count data are reflected in Table B-5 and graphed in
Figure B-2.   Both the 350-mL and 750-mL fuel volumes appear to produce a
larger quantity of small particles when compared to the 525-mL volume data in
Figure B-2.   Based on a comparison of the data in Figures B-1 and B-2, this
evaluation would be very interesting for the other fuels which appear to
produce more small particles after aging than does the Cat 1-H.

TABLE B-4. EFFECT OF VARIOUS FUEL VOLUMES/HEIGHTS ON
D 2274 TEST RESULTS FOR CAT 1-H

Volume, mL	Particulates, mg/100 mL
350*	4.97
525	5.38
	4.29
630*	5.47
750	2.99
	5.22
900*	5.22

* Equivalent fluid column height in tube.

TABLE B-5. AVERAGE PARTICLE COUNT DATA FOR VARIOUS
CAT 1-H FUEL VOLUMES BEFORE AND AFTER FINAL D 2274 FILTRATION
(No. Particles/mL)

Particle Diameter, μm	350 mL			525 mL		
	Before	After	Difference	Before	After	Difference
0.5-0.8	1229000	29300	1200000	429000	470	429000
0.8-1.0	678000	2500	676000	153000	610	152000
1.0-2.0	1091000	5600	1085000	154000	540	153000
2.0-3.0	40500	4800	35700	71400	260	71100
3.0-5.0	1400	830	570	83000	200	82800
>5.0	300	590	-290	125000	230	125000
Calculated wt, mg/L	2.54	0.22		3.38*	0.06	

Particle Diameter, μm	750 mL		
	Before	After	Difference
0.5-0.8	216000	17500	198000
0.8-1.0	784000	6800	777000
1.0-2.0	387000	3500	384000
2.0-3.0	30500	520	30000
3.0-5.0	8000	380	7600
>5.0	2500	410	2100
Calculated wt, mg/L	1.98	0.12	

* Last channel eliminated.
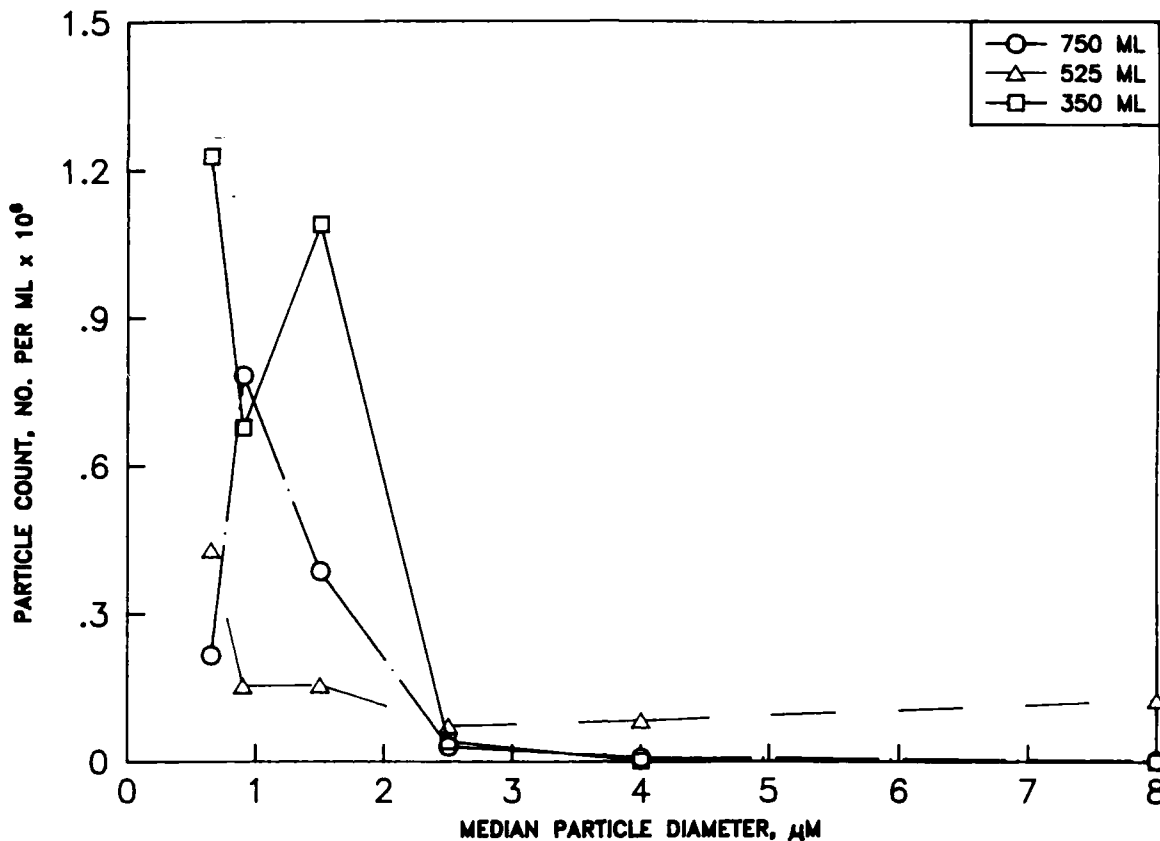
FIGURE B-2. EFFECT OF VARIOUS VOLUMES ON PARTICLE
COUNT AFTER AGING CAT 1-H BUT PRIOR TO FINAL FILTRATIONS

3. Time/Temperature Effects

During an evaluation of time and temperature effects, particle counts for Cat 1-H and the LCO Blend fuel at 16 hours (80°, 95°, and 108°C) were obtained and summarized in Tables B-6 and B-7, respectively. Cat 1-H and LCO Blend fuel data at 95°C for 8, 16 and 24 hours are displayed in Tables B-8 and B-9, respectively. Figures B-3 through B-6 illustrate the particle-size distribution before the final filtration in the fuel aging process for these two fuels.

The number and size of particles formed increased as the temperature increased for the Cat 1-H fuel aged for 16 hours. This could again indicate particle agglomeration. The fact that this agglomeration takes place above

TABLE B-6. PARTICLE COUNT FOR CAT 1-H FUEL AGED 16 HR AT VARIOUS TEMPERATURES BEFORE AND AFTER FINAL FILTRATION (No. Particles/mL)

Particle Diameter, μm	80°C(175°F)			95°C(203°F)		
	Before	After	Difference	Before	After	Difference
0.5-0.8	382000	124000	258000	1229000	29300	1200000
0.8-1.0	19000	9100	10000	678000	2500	676000
1.0-2.0	10800	4500	6300	1091000	5600	1085000
2.0-3.0	4700	1800	2900	40500	4800	35700
3.0-5.0	300	290	10	1400	830	570
>5.0	30	30	0	300	590	-290
Calculated wt, mg/L	0.12	0.06		2.54	0.22	

Particle Diameter, μm	108°C(225°F)		
	Before	After	Difference
0.5-0.8	752000	72900	679000
0.8-1.0	1765000	4000	1761000
1.0-2.0	1760000	2100	1758000
2.0-3.0	229000	1800	227000
3.0-5.0	2900	300	2600
>5.0	30	30	0
Calculated wt, mg/L	52.8	0.04	

TABLE B-7. PARTICLE COUNT FOR LCO BLEND FUEL AGED 16 HR AT VARIOUS TEMPERATURES BEFORE AND AFTER FINAL FILTRATION (No. Particles/mL)

Particle Diameter, μm	80°C(175°F)			95°C(203°F)		
	Before	After	Difference	Before	After	Difference
0.5-0.8	4407000	8157000	-3750000	8101000	35120000	-27020000
0.8-1.0	2510000	2635000	-125000	4685000	2887000	1798000
1.0-2.0	3078000	857000	2221000	2344000	540000	1804000
2.0-3.0	1116000	87700	1028000	248000	48800	199000
3.0-5.0	568000	9500	558000	8300	5000	3300
>5.0	50500	530	50000	2200	2200	0
Calculated wt, mg/L	43.85	4.38		8.99	7.42	

Particle Diameter, μm	108°C(225°F)		
	Before	After	Difference
0.5-0.8	126390000	41090000	85300000
0.8-1.0	20680000	7134000	13550000
0.1-2.0	2346000	760000	1586000
2.0-3.0	228000	5000	223000
3.0-5.0	301000	1800	299000
>5.0	530000	3100	527000
Calculated wt, mg/L	165.8	9.80	

TABLE B-8. PARTICLE COUNT FOR CAT 1-H FUEL AGED AT 95°C (203°F)
FOR VARIOUS TIMES BEFORE AND AFTER FINAL FILTRATION
(No. Particles/mL)

Particle Diameter, μm	8 Hours			16 Hours		
	Before	After	Difference	Before	After	Difference
0.5-0.8	75900	50200	25700	1229000	29300	1200000
0.8-1.0	4800	3500	1300	678000	2500	676000
1.0-2.0	6300	5500	800	1091000	5600	1085000
2.0-3.0	1100	1900	-800	40500	4800	35700
3.0-5.0	210	150	60	1400	830	570
>5.0	70	90	-20	300	590	-290
Calculated wt, mg/L	0.05	0.06		2.54	0.22	

Particle Diameter, μm	24 Hours		
	Before	After	Difference
0.5-0.8	1832000	74600	1752000
0.8-1.0	3435000	13600	3421000
1.0-2.0	643000	4400	639000
2.0-3.0	37000	2400	34600
3.0-5.0	2000	370	1600
>5.0	50	300	-250
Calculated wt, mg/L	2.79	0.12	

TABLE B-9. PARTICLE COUNT FOR LCO BLEND FUEL AGED AT
95°C (203°F) FOR VARIOUS TIME BEFORE AND AFTER FINAL FILTERATION
(No. Particles/mL)

Particle Diameter, μm	8 Hours			16 Hours		
	Before	After	Difference	Before	After	Difference
0.5-0.8	29400000	11950000	17450000	8101000	35120000	-27020000
0.8-1.0	339000	832000	-493000	4685000	2887000	1798000
1.0-2.0	166000	13900	152000	2344000	540000	1804000
2.0-3.0	52000	380	51600	248000	48800	199000
3.0-5.0	36400	260	36100	8300	5000	3300
>5.0	7700	520	7200	2200	2200	0
Calculated wt, mg/L	6.33	1.99		8.99	7.42	

Particle Diameter, μm	24 Hours		
	Before	After	Difference
0.5-0.8	500620000	87940000	512680000
0.8-1.0	23720000	3790000	19930000
1.0-2.0	4041000	329000	3712000
2.0-3.0	921000	42800	878000
3.0-5.0	360000	41400	319000
>5.0	72000	11800	60200
Calculated wt, mg/L	127.1	17.58	

80°C may indicate a region in which there is a change in particle formation mechanisms. This increase was not as dramatic with the LCO Blend fuel. Time at 95°C greatly affected the increase in smaller particles in the Cat 1-H fuel, but seemed to have no effect on the LCO Blend fuel (Figures B-5 through B-6), which seemed to have higher concentrations of smaller particles at shorter time periods. The particle size distribution data in earlier phases of this report were not nearly as consistent as is the data in Table B-6 through B-9, as it relates to families of particles increasing with either time or temperature.
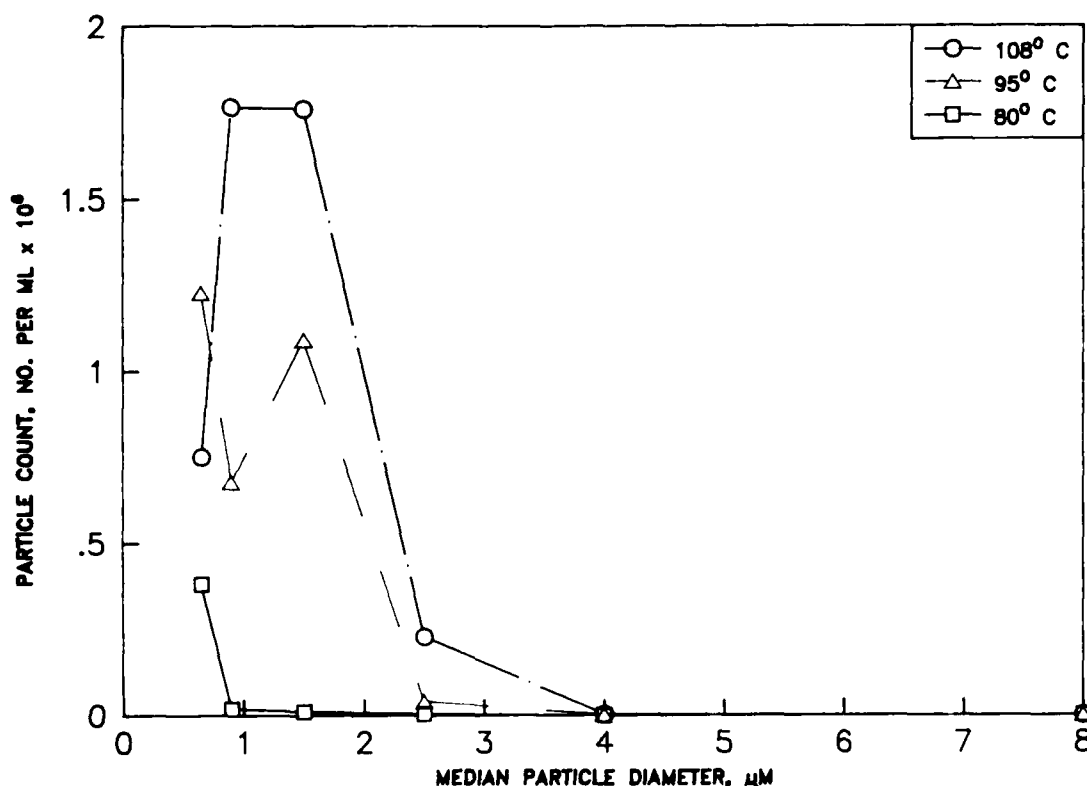
FIGURE B-3. EFFECT OF TEMPERATURE ON PARTICLE COUNT
IN CAT 1-H AFTER AGING 16 HOURS BUT PRIOR TO FINAL FILTRATION
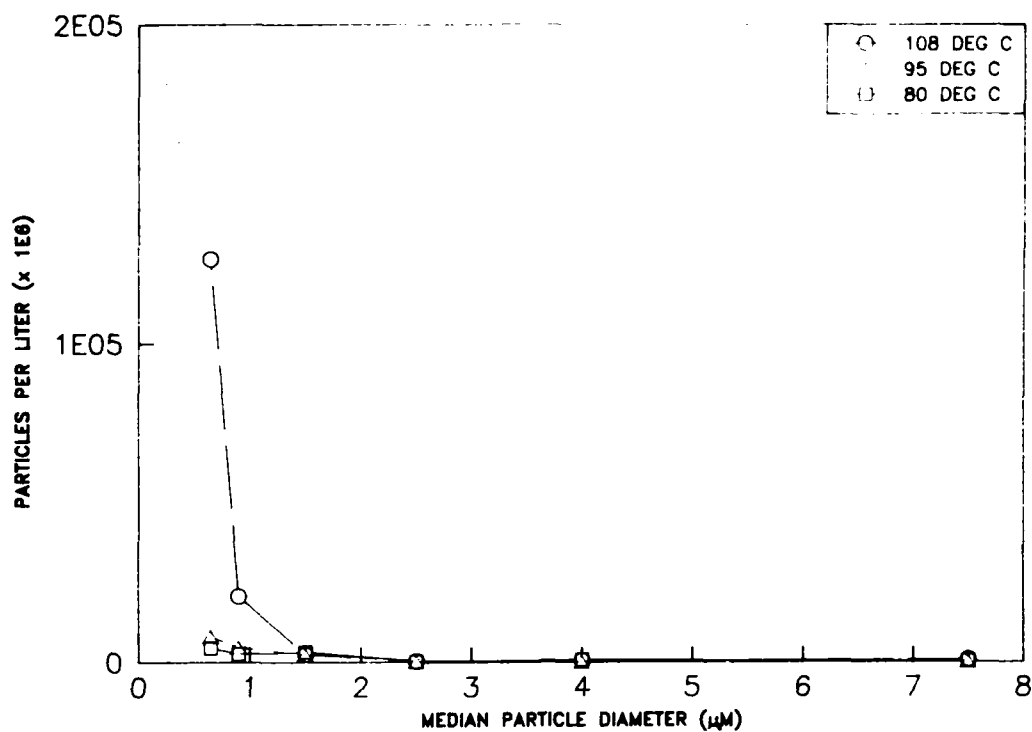
FIGURE B-4. TEMPERATURE EFFECTS ON PARTICLE COUNT IN LCO BLEND
FUEL AFTER AGING 16 HOURS BUT PRIOR TO FINAL FILTRATION

FIGURE B-5. EFFECT OF TIME ON PARTICLE COUNT IN CAT 1-H
AFTER AGING AT 95°C BUT PRIOR TO FINAL FILTRATION
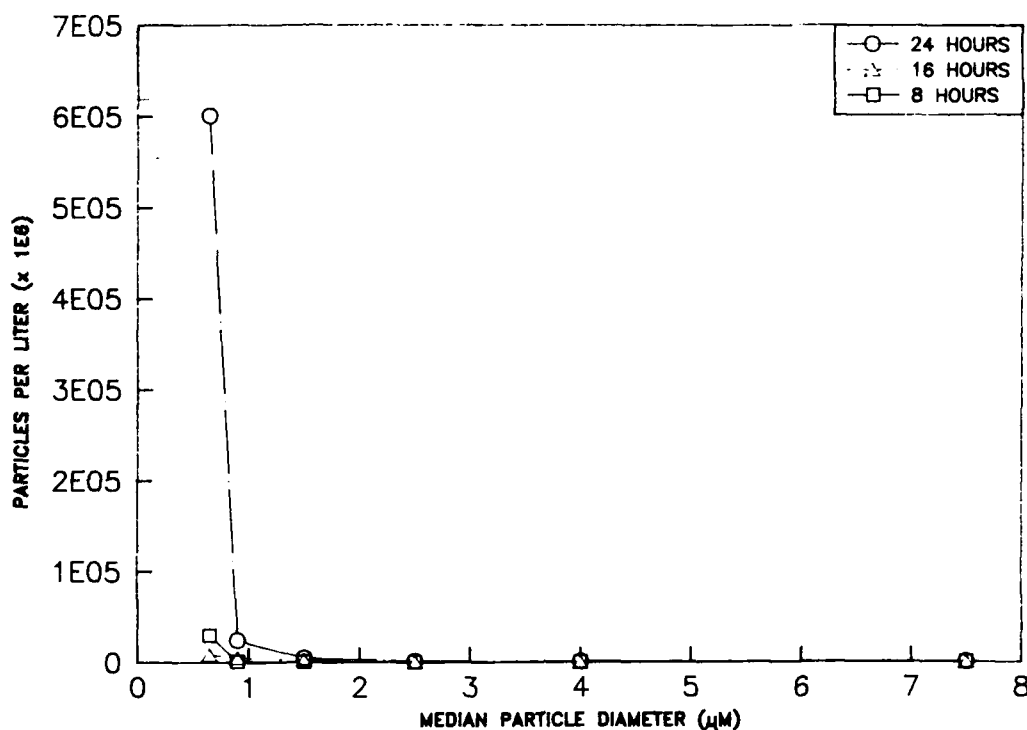
FIGURE B-6. TIME EFFECT ON PARTICLE COUNT IN LCO BLEND
FUEL AFTER AGING AT 95°C BUT PRIOR TO FINAL FILTRATION

4. Effect of Gas Composition and Bubbling Rate

Oxygen (O_2), air, and nitrogen (N_2) flowing at 3 ± 0.3 liters/hr and air at
atmospheric pressure (no flow) for 16 hours were used to determine the effect
of gas composition on D 2274 results for the Cat 1-H and LCO Blend test
fuels. Other than these changes, standard D 2274 techniques were employed.

Particle size distribution data are given in Tables B-10 and B-11 for Cat 1-H
and LCO Blend fuels, respectively. Graphical representations of selected
data are given in Figures B-7 and B-8 for Cat 1-H and LCO Blend fuel, respec-
tively. Again, an increase in particulate size and number is noted for Cat
1-H, particularly with bubbled oxygen indicating particle growth (probably by
agglomeration). There is a similar indication for the LCO Blend fuel, but
not nearly as pronounced. The particle density growth of 1.5 μm medium
diameter particles from a low of 5,500 particles/mL to a high of 1,091,000
particle/mL for bubbling nitrogen and oxygen, respectively, for the Cat 1-H
fuel in Figure B-7 is dramatic.

TABLE B-10. PARTICLE COUNT FOR CAT 1-H FUEL AGED 16 HR IN VARIOUS
ATMOSPHERES BEFORE AND AFTER FINAL FILTRATION (No. Particles/mL)

Particle Diameter, μm	O_2			Air		
	Before	After	Difference	Before	After	Difference
0.5-0.8	1229000	29300	1200000	3488000	316000	3172000
0.8-1.0	678000	2500	676000	496000	22300	474000
1.0-2.0	1091000	5600	1085000	117000	18300	98700
2.0-3.0	49500	4800	44700	15000	7000	8000
3.0-5.0	1400	830	570	380	740	-360
>5.0	300	590	-290	240	310	-70
Calculated wt, mg/L	2.54	0.22		0.99	0.23	

Particle Diameter, μm	N_2			No Bubbling		
	Before	After	Difference	Before	After	Difference
0.5-0.8	493000	356000	137000	1021000	304000	717000
0.8-1.0	19100	13800	5300	1236000	61200	1175000
1.0-2.0	5500	1700	3800	338000	20100	318000
2.0-3.0	2200	30	2200	9600	9800	-200
3.0-5.0	510	0	510	1400	1200	200
>5.0	30	0	30	610	600	10
Calculated wt, mg/L	0.12	0.05		1.35	.35	

TABLE B-11. PARTICLE COUNT FOR LCO BLEND FUEL AGED 16 HR IN VARIOUS
ATMOSPHERES BEFORE AND AFTER FINAL FILTRATION (No. Particles/mL)

Particle Diameter, μm	O_2			Air		
	Before	After	Difference	Before	After	Difference
0.5-0.8	8101000	35120000	-27020000	25430000	2053000	23380000
0.8-1.0	4685000	2887000	1798000	1360000	985000	375000
1.0-2.0	2344000	540000	1804000	161000	22900	138000
2.0-3.0	248000	48800	199000	84000	360	83600
3.0-5.0	8300	5000	3300	92800	200	92600
>5.0	2200	2200	0	92700	140	92600
Calculated wt, mg/L	8.99	7.42		7.42*	0.68	

| Particle Diameter, μm	N_2			No Bubbling		
	Before	After	Difference	Before	After	Difference
0.5-0.8	6027000	3510000	2517000	26580000	2855000	23720000
0.8-1.0	49000	260000	-211000	8500	1300	7200
1.0-2.0	148000	12800	135000	3600	570	3000
2.0-3.0	20900	430	20500	970	210	760
3.0-5.0	13100	170	12900	800	130	670
>5.0	5900	170	5700	600	230	370
Calculated wt, mg/L	3.0	0.61		3.61	0.43	

* Last channel eliminated.
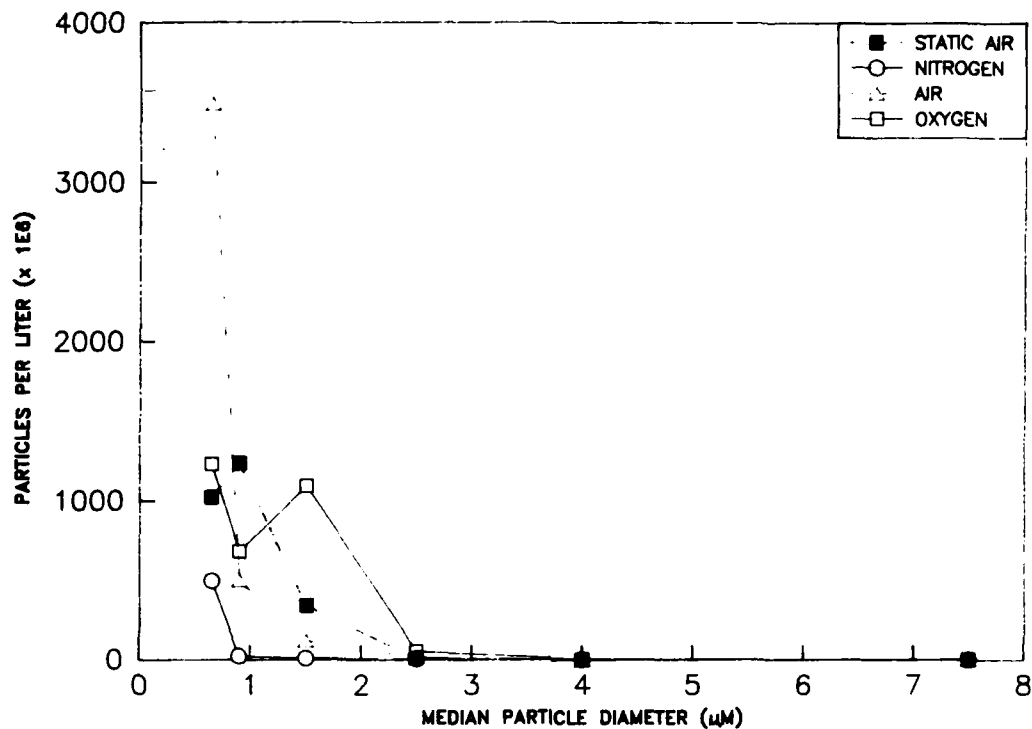
FIGURE B-7.   EFFECT OF ATMOSPHERE ON PARTICLE COUNT IN
CAT 1-H FUEL AFTER AGING 16 HOURS BUT PRIOR TO FINAL FILTRATION
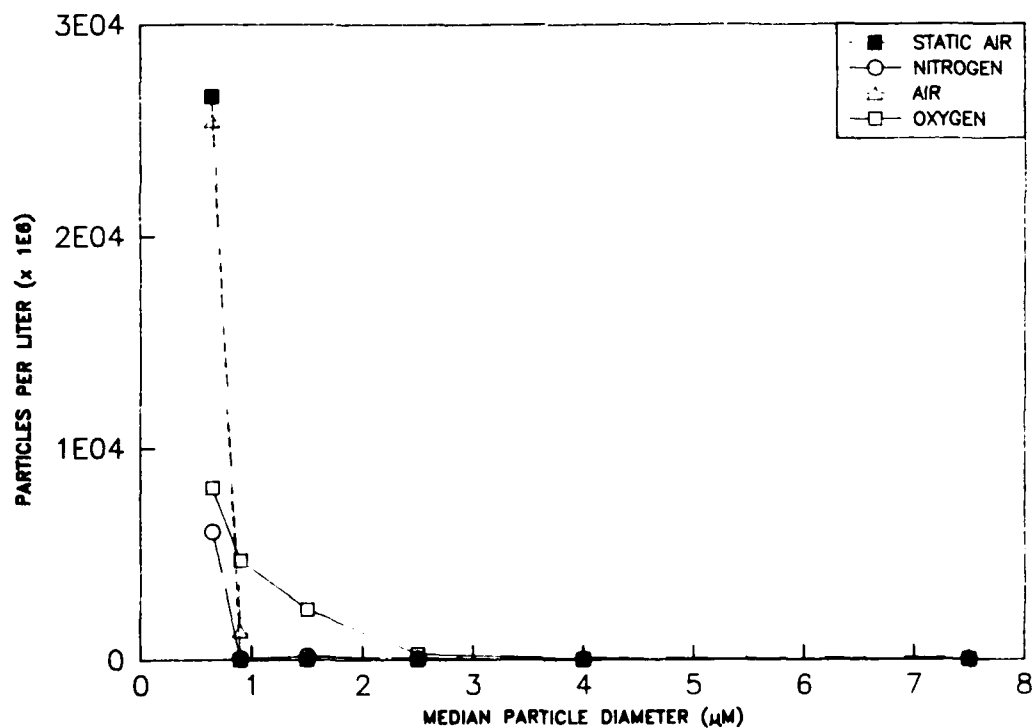
FIGURE B-8.   EFFECT OF ATMOSPHERE ON PARTICLE COUNT IN
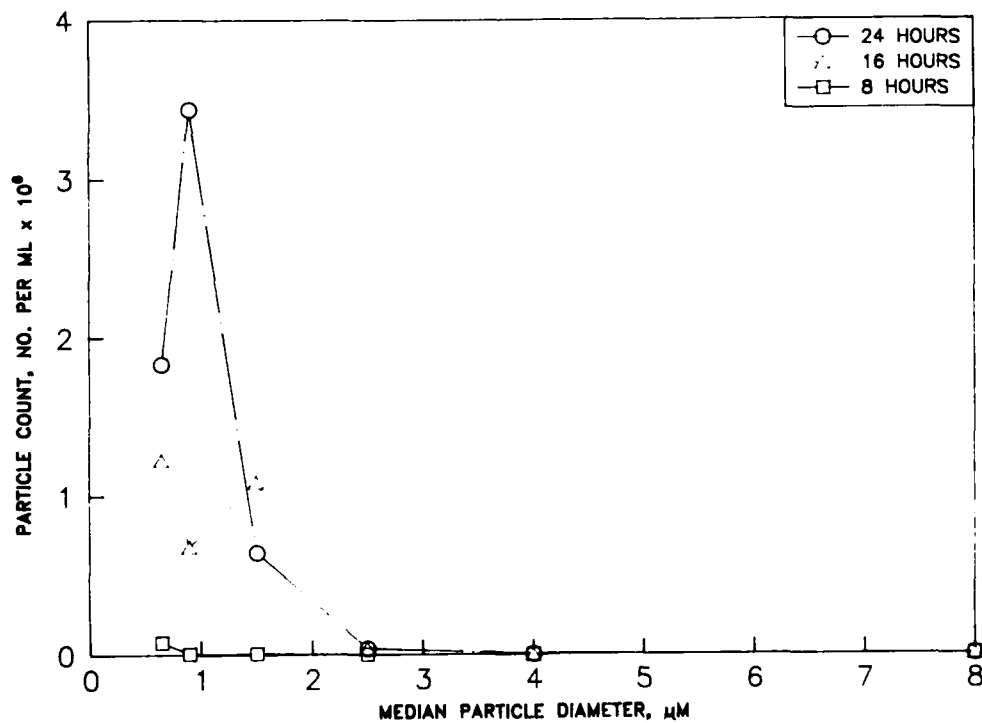LCO BLEND FUEL AFTER AGING 16 HOURS BUT PRIOR TO FINAL FILTRATION

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5. Effect of Cool-Down Times/Temperatures

Table B-12 summarizes filterable insolubles for four test fuels for various cool-down time periods and temperature.

TABLE B-12. EFFECT OF VARIOUS COOL-DOWN TIMES
AND TEMPERATURES ON D 2274 FILTERABLE INSOLUBLES RESULTS

Cool-down Time, Hr	Fuel	Particulates* at Final Temperature, mg/100 mL		
		0°C	Room Temp.	35+°C
2	Cat 1-H	6.55	3.65	5.07
	LCO Blend		2.55	
	1% S		1.45	
	DF-2		2.34	
4	Cat 1-H	2.46	3.9?	5.24
	LCO Blend		2.49	
	1% S	2.53	1.83	
	DF-2		2.70	
6	Cat 1-H	5.59	5.07	

* Particulates = Filterable Insolubles.

Table B-13 and Figures B-9 through B-11 display the particle count and distribution data. Particle agglomeration appears to be a factor at 4- and 6-hour cool down times. It may also be a factor at 0°C in the 2-hour cool down period.

TABLE B-13. PARTICLE COUNT AT VARIOUS COOL-DOWN TIMES/TEMPERATURES
BEFORE AND AFTER FINAL FILTRATION
(No. Particles/mL)

2 Hr - Room Temperature

Particle Diameter, μm	LCO Blend			DF-2		
	Before	After	Difference	Before	After	Difference
0.5-0.8	3945000	1781000	2164000	2761000	2281000	480000
0.8-1.0	3540000	595000	2945000	703000	722000	-19000
1.0-2.0	1293000	901000	392000	450000	451000	-1000
2.0-3.0	63400	4400	59000	37100	0	37100
3.0-5.0	1400	580	820	290	0	290
>5.0	280	420	-140	110	0	110
Calculated wt, mg/L	4.36	2.02		1.62	1.26	

Particle Diameter, μm	1% S			Cat. 1-H		
	Before	After	Difference	Before	After	Difference
0.5-0.8	2478000	4395000	-1917000	174000	19100	155000
0.8-1.0	879000	29100	850000	349000	6600	342000
1.0-2.0	371000	15700	355000	376000	10900	365000
2.0-3.0	6400	7600	-1200	11400	7300	4100
3.0-5.0	1100	1100	0	1700	1800	-100
>5.0	560	610	-50	1400	2000	-600
Calculated wt, mg/L	1.43	.93		1.21	.61	

4 Hr - Room Temperature

Particle Diameter, μm	LCO Blend			DF-2		
	Before	After	Difference	Before	After	Difference
0.5-0.8	8101000	35120000	-27020000	2076000	912000	1164000
0.8-1.0	4685000	2887000	1798000	649000	84700	563000
1.0-2.0	2344000	540000	1804000	1257000	326000	931000
2.0-3.0	248000	48800	199000	4400	148000	-144000
3.0-5.0	8300	5000	3300	3500	1900	1600
>5.0	2200	2200	0	0	0	0
Calculated wt, mg/L	8.99	7.42		2.63	1.81	

Particle Diameter, μm	1% S			Cat 1-H		
	Before	After	Difference	Before	After	Difference
0.5-0.8	4736000	133000	4603000	1229000	29300	1200000
0.8-1.0	259000	7900	251000	678000	2500	676000
1.0-2.0	420000	10300	410000	1091000	5600	1085000
2.0-3.0	34100	4700	29400	40500	4800	35700
3.0-5.0	800	550	250	1400	830	570
>5.0	440	230	210	300	590	-290
Calculated wt, mg/L	1.75	.14		2.54	0.22	

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TABLE B-13. PARTICLE COUNTS AT VARIOUS COOL-DOWN TIMES/TEMPERATURES
BEFORE AND AFTER FINAL FILTRATION
(No. Particles/mL) Cont'd

6 Hr - Room Temperature

Particle Diameter, μm	Cat 1-H		
	Before	After	Difference
0.5-0.8	1731000	12300	1719000
0.8-1.0	565000	2900	562000
1.0-2.0	288000	2600	285000
2.0-3.0	52600	790	51800
3.0-5.0	38500	590	37900
>5.0	32000	750	31200
Calculated wt, mg/L	10.14	.21	

2 Hr - 0°C

Particle Diameter μm	Cat 1-H		
	Before	After	Difference
0.5-0.8	2624000	13900	2610000
0.8-1.0	592000	1400	591000
1.0-2.0	273000	1100	272000
2.0-3.0	38800	340	38500
3.0-5.0	37500	370	37100
>5.0	65900	670	65200
Calculated wt, mg/L	18.29	.18	

4 Hr - 0°C

Particle Diameter, μm	1%S			Cat 1-H		
	Before	After	Difference	Before	After	Difference
0.5-0.8	3220000	287000	2933000	350000	209000	141000
0.8-1.0	720000	5900	714000	288000	3100	285000
1.0-2.0	372000	11000	361000	331000	7400	324000
2.0-3.0	14400	4900	9500	7900	4400	3500
3.0-5.0	1300	560	740	650	640	10
>5.0	710	450	260	360	410	-50
Calculated wt, mg/L	1.57	.32		.84	.19	

6 Hr - 0°C

Particle Diameter, μm	Cat 1-H		
	Before	After	Difference
0.5-0.8	4131000	41300	4090000
0.8-1.0	1406000	7300	1399000
1.0-2.0	1092000	4100	1088000
2.0-3.0	163000	850	162000
3.0-5.0	116000	720	115000
>5.0	109000	1100	108000
Calculated wt, mg/L	33.75	.31	

TABLE B-13. PARTICLE COUNTS AT VARIOUS COOL-DOWN TIMES/TEMPERATURES
BEFORE AND AFTER FINAL FILTRATION
(No. Particles/mL) Cont'd

2 Hr - 35+°C

Particle Diameter, μm	Cat 1-H		
	Before	After	Difference
0.5-0.8	4183000	34900	4148000
0.8-1.0	2460000	1100	2459000
1.0-2.0	435000	150	435000
2.0-3.0	17600	80	17500
3.0-5.0	4300	120	4200
>5.0	10900	690	10200
Calculated wt, mg/L	4.97	0.18	

4 Hr - 35+°C

Particle Diameter, μm	Cat 1-H		
	Before	After	Difference
0.5-0.8	1894000	80200	1814000
0.8-1.0	542000	6300	536000
1.0-2.0	705000	2700	702000
2.0-3.0	62900	630	62300
3.0-5.0	23000	530	22500
>5.0	5900	1300	4600
Calculated wt, mg/L	4.13	0.35	
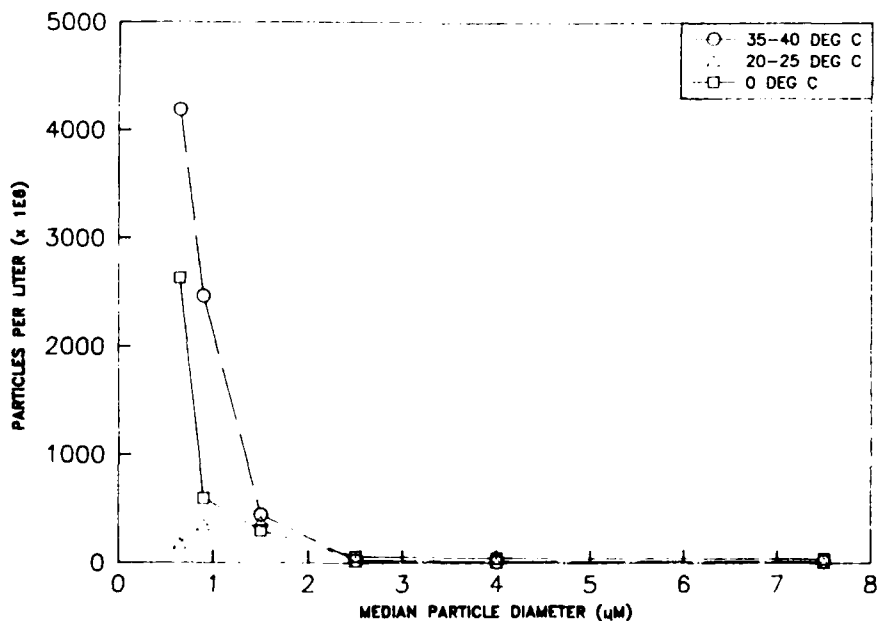
FIGURE B-9. EFFECT OF VARIOUS COOL-DOWN TEMPERATURES
(2 HR) IN CAT 1-H FUEL AFTER AGING BUT PRIOR TO FINAL FILTRATION
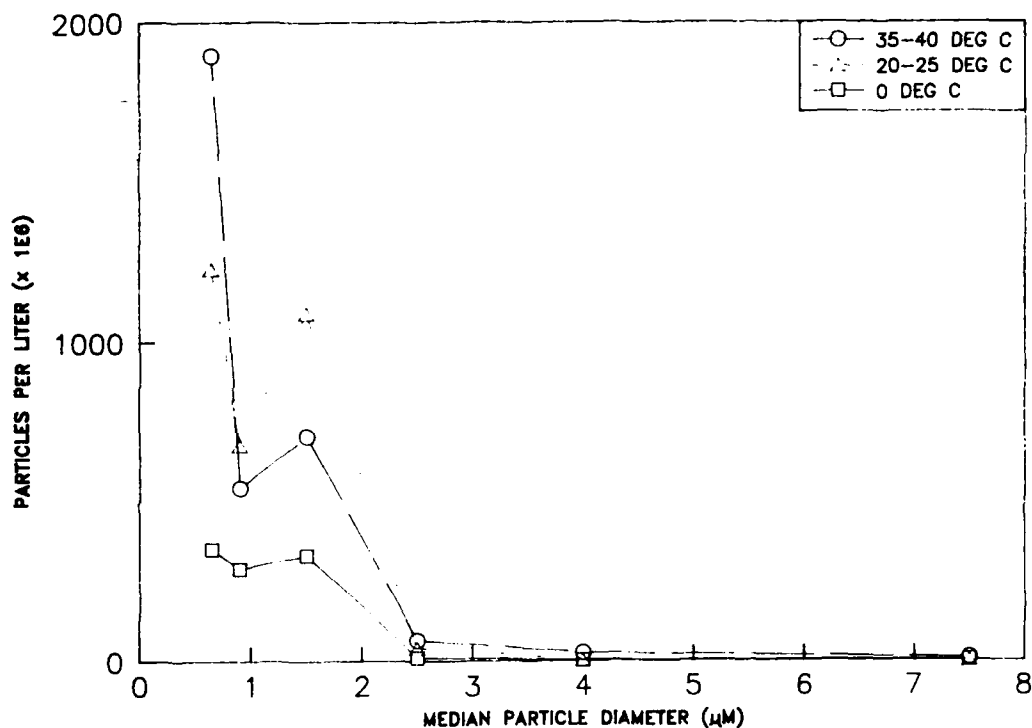
FIGURE B-10.   EFFECT OF VARIOUS COOL-DOWN TEMPERATURES
(4 HR) IN CAT 1-H AFTER AGING BUT PRIOR TO FINAL FILTRATION
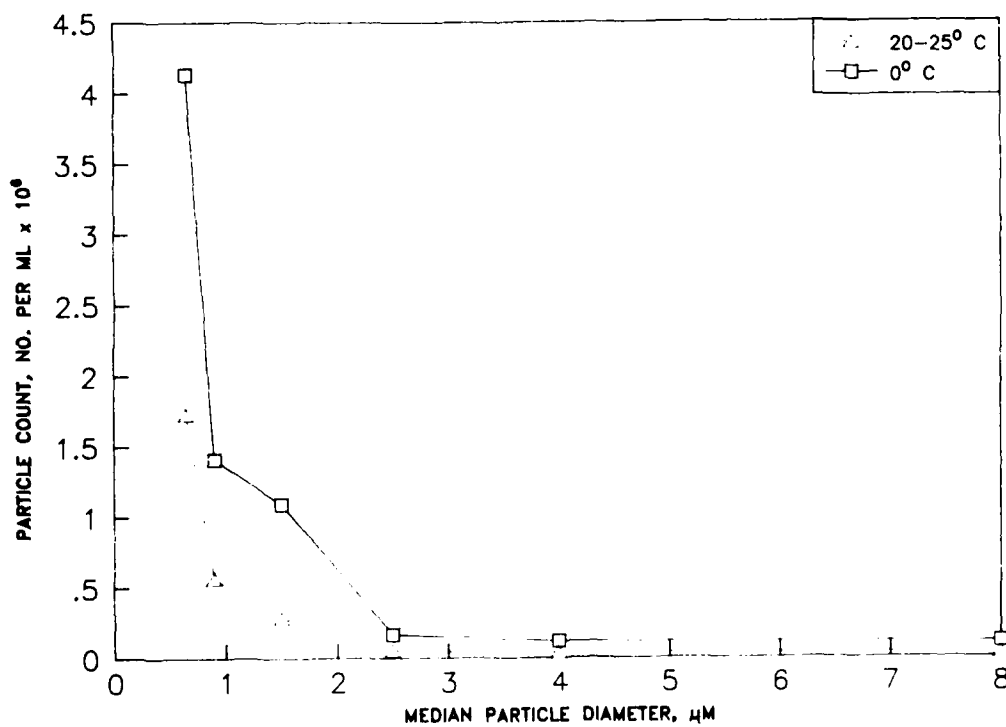
FIGURE B-11.   EFFECT OF VARIOUS COOL-DOWN TEMPERATURES
(6 HR) IN CAT 1-H AFTER AGING BUT PRIOR TO FINAL FILTRATION

APPENDIX C

TEST METHOD FOR OXIDATION STABILITY OF DISTILLATE
FUEL OIL AS USED FOR ROUND-ROBIN TESTING

(Revised 6 February 1985)

The following document contains the suggested procedure for round-robin evaluation. It is not a recommended protocol to evaluate oxidation stability of middle distillate fuel oils.

1.   SCOPE

1.1 This method describes the measurement of inherent stability of middle distillate petroleum fuel under accelerated oxidizing conditions.

1.2 The precision values for this method were developed using middle distillate, petroleum fuels with end point temperatures to be determined. Therefore, this method is applicable only to such mid-distillate fuels. Fuels conforming to ASTM D 396 Grade No. 2, D 975 Grade No. 2-D, and D 2880 Grade No. 2-GT would fall within this limitation.

1.3 All fuels developed from nonpetroleum sources, or containing residuals, are not covered in this method.

CAUTION: This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whomever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2.   APPLICABLE DOCUMENTS

2.1 ASTM Standards

> D 381 Existent Gum in Fuels by Jet Evaporation
> D 2276 Particulate Contaminant in Aviation Turbine
>   Fuels.[1]
> D 2886 Test for Knock Characteristics of Motor Fuels by
>   the Distribution Octane Number (DON) Method, Annex
>   A2, Table 34.[2]
> D 4057 Practice for Manual Sampling of Petroleum and
>   Petroleum Products.[3]

2.2 Other Standards

> American Chemical Society, "Reagent Chemicals," 6th Ed.
>   (1981).
>
> ASTM RR-D2-1012 "Membrane Approval Procedure Referred
>   to in ASTM D 2276, Test for Particulate Contaminant
>   in Aviation Turbine Fuels"

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1) 1983 Annual Book of ASTM Standards, Vol. 05.02.
2) 1983 Annual Book of ASTM Standards, Vol. 05.04.
3) 1983 Annual Book of ASTM Standards, Vol. 05.03.

3. TERMINOLOGY

Adherent Insolubles (formerly Adherent Gum) -- material produced in the course of stressing distillate fuel under the conditions of this test and which adheres to the glassware after fuel has been flushed from the system.

Distillate Fuel -- To be defined.

Filterable Insolubles -- material produced in the course of stressing distillate fuel under the conditions of this test that remains suspended in the fuel or which is easily removed from the oxidation cell and oxygen delivery tube with hydrocarbon solvent and is capable of being removed from the liquids by filtration.

Inherent Stability -- To be defined.

Total Insolubles -- sum of the adherent and filterable insolubles.

Trisolvent -- (TAM), a solution of equal volumes of toluene, acetone, and methanol.

4. SUMMARY OF METHOD

4.1 A 350 mL volume of filtered middle distillate fuel is aged at 95°C (203°F) for 16 hours while oxygen is bubbled through the sample at a rate of 3 liters per hour. After aging, the sample is cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity. Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent. The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed as mg/100 mL, is reported as total insolubles.

5. SIGNIFICANCE AND USE

5.1 The result of this test is a measure of the inherent resistance of a middle distillate fuel to oxidation.

5.2 The method may not provide a prediction of the quantity of insolubles that will form in field storage over any given period of time. The amount of insolubles formed in such field storage is subject to the specific conditions which are too variable for this method to predict accurately.

6. INTERFERENCES

6.1 Oxidation is a major chemical process causing adherent and filterable insolubles to form. Any substance such as copper or chromium that catalyzes oxidation reactions will cause greater quantities of insolubles to form. Since the apparatus used in this test can also be used in ASTM D 943 Test for Oxidation Characteristics of Inhibited Mineral Oils, where coils of copper and steel are used, it is important that any residues that could contain these metals be eliminated from the apparatus by thorough cleaning prior to use. Similarly, to preclude the presence of chromium ions, as well as to protect laboratory personnel from potential harm, chromic acid should not be used for cleaning glassware in the practice of this method.

6.2 It has been found that commercial grades of acetone, if used in the trisolvent, can have impurities which cause an apparently greater level of adherent insolubles to be measured. It is, therefore, critical that only reagent (or higher) grade materials be used in preparing the trisolvent mixture.

6.3 Ultraviolet light exposure has been found to increase the amount of total insolubles. Therefore, the fuel being tested must be shielded from direct exposure to ultraviolet light (sunlight or fluorescent). Conduct all sampling, measuring, filtration, and weighing away from direct sunlight and in as dark an area as would be compatible with other laboratory operations. Storage before stress, the stress period and cool-down after stressing shall be in the dark.

7. Apparatus [4]

7.1 Oxidation Cell, of borosilicate glass, as shown in Figure 1, shall consist of a test tube, condenser, and oxygen delivery tube. [5]

7.2 Heating Bath, with a thermostatically controlled liquid medium, shall be capable of maintaining the bath temperature at 95 ± 0.2°C (203 ± 0.4°F). It shall be fitted with a suitable stirring device to provide a uniform temperature throughout the bath. It shall be large enough to hold the desired number of oxidation cells immersed to a depth of approximately 350 mm. Further, the bath construction must permit shielding the fuel samples in the oxidation cells from light while they are undergoing oxidation. [6]

7.3 Flowmeters, shall have a capability of measuring 3 ± 0.3 liters/h of oxygen. One flowmeter shall be provided for each oxidation cell.

7.4 Drying Oven, shall be capable of safely evaporating the solvent at 80°C ± 2°C (175°F ± 5°F) for the drying of filter materials.

7.5 Drying Oven, shall be capable of drying glassware at 105°C±5°C (220±10°F).

7.6 Filter Assembly, shall be capable of holding the filters described in Section 7.7.

7.7 Filter Media [7], 47 mm diameter cellulose ester screen filters with a nominal pore size of 0.8 micrometers. Single filters will be used for prefiltration, however, a matched weight pair 0.8 micrometer filters must be used for determination of filterable particulates.

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4) It is mandatory that all equipment be calibrated according to manufacturer's instructions on a periodic basis to assure consistency of results.
5) The dimensions in Figure 1 are identical with the dimensions in Figure 1 of ASTM Method D943, Test for Oxidation Characteristics of Inhibited Steam-Turbine Oils, found in the Annual Book of ASTM Standards, Vol. 05.01.
6) List of manufacturers available from ASTM Hq. Philadelphia.
7) Filters shall be qualified using ASTM RR-D2-1012 procedure. This procedure and a list of qualified vendors may be obtained from ASTM Headquarters, Philadelphia, PA.

7.8 Evaporating Vessel, borosilicate glass beaker, 200 mL capacity, tall style.

7.9 Hot Plate, capable of heating a liquid in the evaporating vessel (7.8) to 135°C (275°F).

8.   REAGENTS AND MATERIALS

8.1 Purity of Reagents, Reagent grade (or better) chemicals shall be used in all tests.   Unless otherwise indicated, it is intended that all reagents conform to specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[8]

8.2 Trisolvent, a mixture of equal volumes of acetone, methanol, and toluene.   See 8.1.   (See also Annex A1 for safety and handling information).

CAUTION: It is particularly important that technical, commercial, practical, or industrial grades (however they are designated by the particular manufacturer) shall not be used, as their use may lead to apparently increased levels of adherent gum.

8.3 Isooctane, isooctane of ASTM knock test reference fuel grade, prefiltered through filter media as described in Section 7.7.   (See Annex A1 for safety and handling information).

8.4 Oxygen, 99.5 percent purity or better.   When the oxygen is delivered through a plant system of piping, a filter shall be provided adjacent to the constant temperature bath to prevent the introduction of line debris or moisture into the oxidation cells; a pressure regulator adequate to maintain a constant flow of gas through the apparatus shall also be used.   A tank of oxygen of
the specified purity may be used if it is equipped with a two-stage pressure regulator.

> Warning! Oxygen vigorously accelerates
> combustion. Equipment having exposed
> surfaces containing oil or grease should
> not be used. (See Annex A1 for safety
> and handling information).

9.   SAMPLES AND SAMPLING

9.1 Fuel samples should be analyzed as soon as possible after receipt.   If a fuel cannot be tested within one day, it is recommended that it be blanketed

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8) "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC.   For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by J. Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

with an inert gas such as zero nitrogen, argon, or helium and stored at a temperature no higher than 10°C (50°F) but not lower than the cloud point. (See Appendix 1)

CAUTION: Plastic containers are not acceptable for sample storage due to the potential for leaching of plasticizers. Samples received in such containers should be transferred immediately to an acceptable container, preferably metal cans previously cleaned according to ASTM D 4057. Borosilicate glass containers may be used if they are wrapped or boxed to exclude light. Soft (soda) glass containers should not be used.

10. PREPARATION OF APPRATUS

10.1 Preparation of Glassware, Rinse all glassware thoroughly with trisolvent followed by water then wash with a mildly alkaline or neutral laboratory detergent. Rinse with deionized or distilled water followed by acetone. (See Annex A1 for safety and handling information)

10.2 Oxidation Cells, After completion of Section 10.1, fill oxidation cells with the recommended concentration of the laboratory detergent in water. Place the oxygen delivery tube in the oxidation cell, place the condencer over the oxygen delivery tube and allow to soak at least two hours. Wash, drain, then rinse five times with tap water followed by three rinses with distilled or deionized water. Rinse with acetone; drain and allow the oxidation cell and oxygen delivery tube to dry.

10.4 Preparation of Evaporating Beakers, Dry the 200 mL cleaned beakers (Section 10.1) for 1 hour in an oven at 105°±5°C (220±10°F). Place the beakers in a desiccator (without desiccant) and allow to cool for 1 hour. Weigh beakers to the nearest 0.1 mg.

11. PROCEDURE

11.1 Sample Preparation, Place one filter (described in Section 7.7) on the filter support and clamp the filter funnel to the support as shown in Figure 2. Apply suction (approximately 80 kPa [12 psi]). Pour 400 mL of the fuel through the filter (see Section 7.7) into a clean (paragraph 10.1) 500 mL glass suction flask. Repeat preparation for each sample to be run. After filtration is complete, the filter media may be discarded. Never use the same filters for a second increment of fuel, because any material deposited on the filters by a previous increment of fuel may result in a greater removal of solids from the next increment.

11.2 Assembling the Oxidation Apparatus, Place a clean oxygen delivery tube into a clean oxidation cell (Section 10) and pour 350 ± 5 mL of the filtered fuel into the cell. As soon thereafter as possible, but in no case greater than one hour after measuring the fuel, immerse the test cell in the 95°C (203°F) heating bath. During any interim period the cell shall be stored in the dark. The level of fuel in the oxidation cell should be below the level of the liquid medium in the heating bath. Place a condenser over the oxygen delivery tube and oxidation cell; connect the condenser to the cooling water. Connect the oxygen delivery tube to the oxygen supply through the flowmeter and adjust the oxygen flow to 3 ± 0.3 liters/h. Make sure samples

are protected from light. Record the time the oxidation cell was placed in the bath and allow the oxidation cell to remain in the bath for 16 hours ± 1/4 hour.

11.3 <u>Cooling the Sample</u>, Remove the sample(s) from the heating bath and place in a dark, ventilated site at room temperature which must be above the cloud point of the fuel (24±5°C, 75 ± 10°F) until room temperature is attained or for no longer than 4 hours.

11.4 <u>Filterable Insolubles</u>, Assemble the filter apparatus as illustrated in Figure 2, using one set of matched pair filters.
Apply suction (approximately 80 kPa [12 psi]); pour the cooled sample through the filter. On completion of filtration, <u>completely</u> rinse the oxidation cell and oxygen delivery tube with three 50 ± 5 mL volumes of isooctane. Pass all rinsings through the filter assembly. After filtration is complete, disconnect the top part of the filter assembly, and wash down the rim of the filter media and surrounds with a further 50 ± 5 mL of isooctane. Discard the filtrate. Dry, at 80°C (175°F), cool (30 minutes) and weigh the upper (sample) and lower (blank) filters separately to the the nearest 0.1 mg.

NOTE 1 -- If the filtration of the sample cannot be completed within 2 hours as a result of severe filter plugging, filter the remaining fuel through a separate set of filters.

11.6 <u>Adherent Insolubles</u>, After final rinsing of the oxidation cell and oxygen delivery tube with isooctane, dissolve any adherent insolubles from the surfaces of these pieces using three rinses of about 25 mL each of tri-solvent. The oxidation cell and oxygen delivery tube should be examined for evidence of stain or color indicating incomplete removal. If such stain or color is noted, rinse with a fourth 25 mL volume of trisolvent.

ROUND-ROBIN OPTION 1, <u>Hot plate method</u>, Collect the rinsings in a tared 200 mL tall beaker. Place the beaker and contents on a hot plate; heat the liquid to 135°C (275°F) and evaporate the trisolvent under a hood with a stream of dry nitrogen (or other inert gas).

CAUTION: There is a chance for boiling/splashing of the liquid outside of the container.

When all the solvent has been evaporated, place the tared beaker containing adherent insolubles in a desiccator (without desiccant) to cool for 1 hour. An adherent insolubles blank should be run on a volume of trisolvent equal to that used in the test. When dry and cool, weigh the tare and sample beakers to the nearest 0.1 mg.

ROUND ROBIN OPTION 2, Evaporate the trisolvent at 160°C (320°F) by the air jet method described in ASTM D 381.

ROUND ROBIN OPTION 3, Run separate tests using both Option 1 and Option 2.

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12. CALCULATIONS

12.1 Calculate the filterable insolubles weight (A) in milligrams per 100 mL. Subtract the weight of the blank (bottom) filter W1 from that of the sample (top) filter W2 (paragraph 11.5) and divide by 3.5.

$$A = \frac{W2-W1}{3.5}$$

12.2 OPTION 1, Calculate the adherent insolubles weight (B) in milligrams per 100 mL. Subtract the tare weight of the blank (W3) and sample (W4) beakers from their final weights (W5), (W6) respectively. Subtract the weight of the blank from the corrected weight of the adherent insolubles (paragraph 11.6) and divide by 3.5.

$$B = \frac{(W6-W4)-(W5-W3)}{3.5}$$

Where:

W3 = tare weight of the blank beaker
W4 = tare weight of the sample beaker
W5 = final weight of the blank beaker
W6 = final weight of the sample beaker

OPTION 2, Since there is no blank beaker, the above formula reduces to $B = \frac{W6-W4}{3.5}$

12.3 Calculate the total insolubles weight (C) in milligrams per 100 mL as the sum of the filterable insolubles (A) and the adherent insolubles (B).

13. REPORT

13.1 Report total insolubles (C) in mg/100 mL.

13.2 A report of filterable insolubles (A), and the adherent insolubles (B) is optional. Reported units should be in mg/100 mL.

14. PRECISION

14.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

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14.2 Repeatability - duplicate results by the same operator should be considered suspect if they differ by more than the following:

(To be determined by a new round-robin)

14.3 Reproducibility - the results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

(To be determined by a new round-robin)
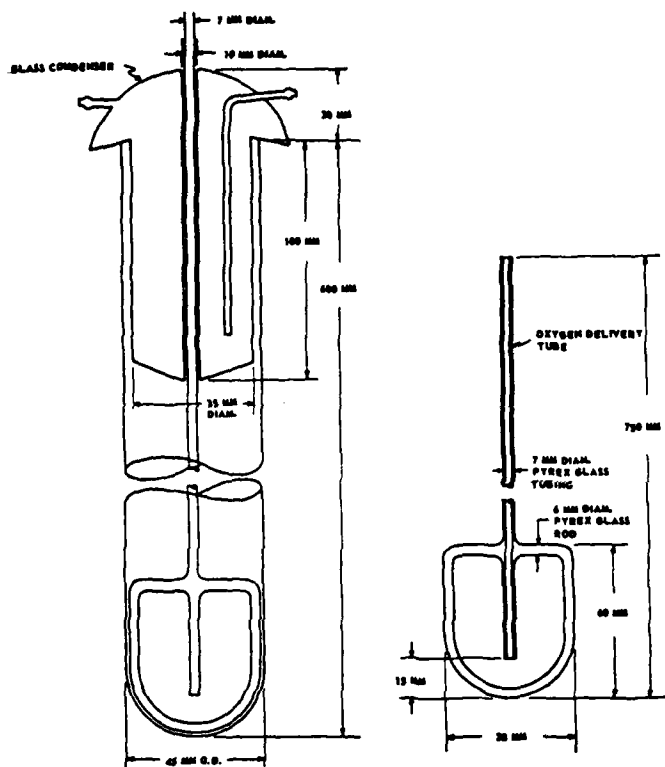
FIGURE 1. OXIDATION CELL.
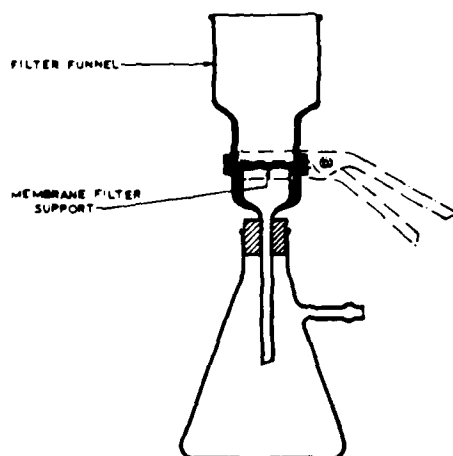
FIGURE 2. APPARATUS FOR DETERMINING TOTAL CONTAMINANT---
BOTTLE SAMPLES.

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ANNEX 1

MANDATORY INFORMATION

A1. PRECAUTIONARY STATEMENTS

A1.1 SCOPE

A1.1.1   This Annex addresses precautions the user of the standard should use in the handling of several reagents, chemicals, solvents, and gases required by the standard. Specifically, this Annex addresses precautions that should be followed in handling acetone, trisolvent, isooctane, methanol (methyl alcohol), oxygen, precipitation naphtha, and toluene.

A1.1.2   This Annex does not purport to address all of the safety problems associated with the use of the standard. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

A1.2 SPECIFIC PRECAUTIONS

A1.2.1   Acetone

Danger! Extremely flammable. Vapors may cause flash fire.

- Keep away from heat, sparks, and open flame.
- Keep container closed.
- Use with adequate ventilation.
- Vapors may spread long distances and ignite explosively.
- Avoid buildup of vapors, and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters.
- Avoid prolonged breathing of vapor or spray mist.
- Avoid contact with eyes or skin.

A1.2.2   Trisolvent

Danger! Extremely flammable. Vapors harmful. May cause flash fire.

- Keep away from heat, sparks, and open flame.
- Keep container closed.
- Use with adequate ventilation.
- Avoid buildup of vapors and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters.
- Avoid breathing of vapor or spray mist.
- Avoid contact with eyes and skin.
- Vapors may travel long distances and ignite explosively.
- Very harmful. May be fatal or cause blindness is swallowed or inhaled.
- Do not take internally.

A1.2.3   Isooctane

Danger! Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.

- Keep away from heat, sparks, and open flame.
- Keep container closed.
- Use with adequate ventilation.
- Avoid buildup of vapors and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters.
- Avoid prolonged breathing of vapor or spray mist.
- Avoid prolonged or repeated skin contact.

A1.2.4   Methanol (methyl-alcohol)

Danger! Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made non-poisonous

- Keep away from heat, sparks, and open flame.
- Keep container closed.
- Avoid contact with eyes and skin.
- Avoid breathing of vapor or spray mist.
- Use with adequate ventilation.
- Do not take internally.

A1.2.5   Oxygen

Warning! Oxygen vigorously accelerates combustion.

This test requires oxygen to contact a combustible material, the fuel. Never allow the oxygen pressure entering the oxidation cell to reach levels much above the atmospheric pressure!

- Always use a pressure regulator. Release regulator tension before opening cylinder valve.
- All equipment and containers used must be suitable and recommended for oxygen service.
- Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.
- Do not mix gases in cylinders.
- Do not drop cylinder. Make sure cylinder is secured at all times.
- Keep cylinder valve closed when not in use.
- Stand away from outlet when opening cylinder valve.
- For technical use only. Do not use for inhalation purposes.
- Keep cylinder out of sun and away from heat. Keep cylinder from corrosive environment. Do not use cylinder without label.
- Do not use dented or damaged cylinders.
- See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.
- Use only in well-ventilated area.

A1.2.6   Toluene

Warning! Flammable. Vapor harmful.

- Keep away from heat, sparks, and open flame.
- Keep container closed.
- Use with adequate ventilation.
- Avoid breathing of vapor or spray mist.
- Avoid prolonged or repeated contact with skin.
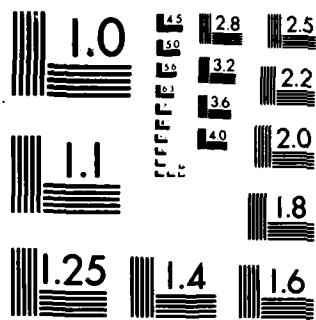
MICROCOPY RESOLUTION TEST CHART

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APPENDIX 1

FUEL SAMPLING

When sampling, the principles of ASTM D 4057 should be used. Every effort must be taken to maintain the representative nature of the sample throughout subdivision into test sample aliquots.

A.1 __Test Samples__, Reduction of the laboratory sample to test sample size (about 400 mL for each determination) depends upon the size of sample received by the laboratory. If the laboratory sample is stored in a tank, drum, or 5-gallon (19-L) or larger can, the pertinent procedures of ASTM D 4057 should be used. Smaller laboratory samples should be thoroughly mixed by shaking, rolling, or other techniques before taking an aliquot portion by pouring, pipetting, or other means. Any tube, thief, pipette, beaker, or other substance that is to contact the laboratory sample should be cleaned with trisolvent and rinsed with a portion of the sample prior to use. Samples that have been stored at temperatures much below 10°C (50°F) should be allowed to warm to room temperature prior to taking an aliquot, thus allowing any separated wax to redissolve and to allow the viscosity to decrease to a point where mixing is effective.

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